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A
MANUAL
OF
CHEMISTRY.

BY
WILLIAM THOMAS BRANDE, F.R.S. L. & E.
OF HER MAJESTY'S MINT;

FELLOW OF THE UNIVERSITY OF LONDON; PROFESSOR OF CHEMISTRY IN THE ROYAL INSTITUTION
OF GREAT BRITAIN, AND TO THE SOCIETY OF APOTHECARIES OF THE CITY OF LONDON;
PRESIDENT OF THE CHEMICAL SOCIETY OF LONDON;
&c., &c., &c.

VOLUME I.

CONTAINING

PART I. THE POWERS OF MATTER,
AND THE
NON-METALLIC ELEMENTS.

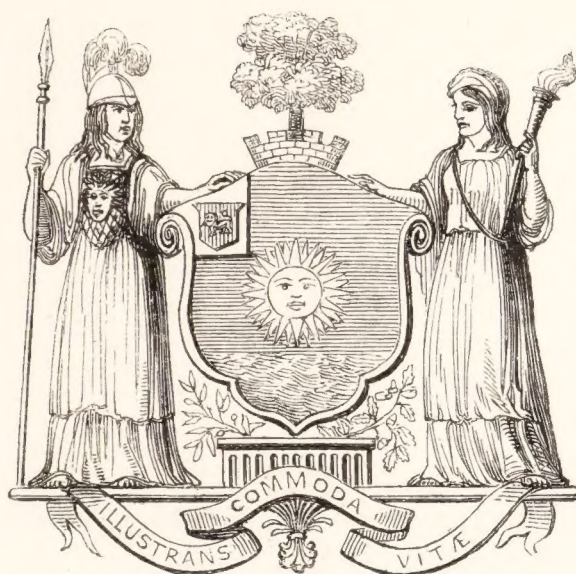
PART II. CHEMISTRY OF THE METALS.

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TO
THE PRESIDENT
AND
MEMBERS
OF
THE ROYAL INSTITUTION OF GREAT BRITAIN,
THIS CONTRIBUTION TO CHEMICAL SCIENCE
IS DEDICATED
BY THEIR FAITHFUL SERVANT,
THE AUTHOR.



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PREFACE.

THIS Work was originally intended as a text-book for the use of the Chemical Students in the Royal Institution, but the reception of the first edition by the Public, its translation into French, German, and Italian, and its republication in America, induced me to endeavor to render it more worthy of such marks of approbation, and accordingly it has been enlarged and improved in several successive Editions. I hope that it now contains a faithful outline of the present state of Chemistry, adapted for the instruction of the beginner, and for the use of the Student in this delightful branch of Experimental Philosophy: writing therefore for the uninitiated, and for the learner, much has been sacrificed to perspicuity, and to simplicity of detail. I must at the same time observe, that Chemistry is not what it was; that with whatever intention the pupil enters upon its study, it will require labor and thought to become usefully acquainted even with its elementary details; and that to reap advantages from its application, either to the purposes of the multitudinous Arts which are dependent upon it, or to the extension of the Sciences which are leagued with it, will perhaps demand more time and study than he is aware of. I believe that the depths of Chemistry are, with the aids which it now enjoys, more easily fathomed than those of most other branches of Physical Science, and am certain that it is admirably calculated to awaken, and to gratify curiosity, in regard to the phenomena both of Nature and of Art; but it is not now, as formerly, the bare history “of the effects of heat and mixture;” those who enter seriously upon its study must be prepared for some intellectual exertion and mental labor: they will then find that its connexion with other Sciences, with the arts of life, and with the phenomena

of nature, is such, as to render it at once useful and popular, and an essential in the range of a liberal education.

But, though chiefly addressed to the Student, I am not without hope that this Manual will be approved by the practical and experimental Chemist, especially by the Teacher of the Science: to such, I have endeavored to recommend it, by copious references to authorities, and by abstracts of practical directions. Should it in these respects prove a work of reference worthy of occasional consultation, another object will be answered.

In consequence of the popular applications of Chemistry, and its extensive connexion with the useful and ornamental Arts, and with the Sciences at large, the general reader finds it often forced upon him; its terms are of frequent occurrence, and its language is in daily use: I have, therefore, added to this Work, a copious Index, intended in some measure to supply the place of a Chemical Dictionary.

In conclusion, I have to observe, that the note-books of my Lectures have served as the foundation of the present volume, and that these include a miscellaneous collection of original and borrowed information: although, therefore, I have endeavored, as far as possible, to refer to authorities, and to cite the sources of my statements, I fear that I may often have unintentionally omitted such acknowledgments. The systematic and elementary works which I have principally consulted, are those of Dr. William Henry, Dr. Thomas Thomson, Dr. Edward Turner, Professor Daniell, and Professor Graham; and of Berzelius, Dumas, Gmelin, Mitscherlich, Thenard, Liebig, and Löwig; and the Dictionaries of Messrs. Aikin, and Dr. Ure; together with the Transactions of the Royal Society, and the English and Foreign Journals; among the latter, the *Annales de Chimie et Physique*, the *Journal de Chimie et Pharmacie*, Poggendorff's *Journal*, and Liebig's *Annalen der Chemie und Pharmacie*, are especially rich in original Chemical information.

The general method which I have adopted, of representing the Atomic, Equivalent, and Percentage composition of bodies, is that originally employed by Leopold Gmelin in his excellent *Handbuch der Theoretischen Chemie*; it saves repetition, and brings much information before the eye of the Student, in a clear but

condensed form; I insert the following statement of the composition of Nitrous Oxide, as an explanatory specimen of one of these tables, in its most general and extended form.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
	A.	E.	Pr.Cent.	Davy.	Berzelius.	Higgins.	Vols.	Sp.Gr.	100 C.I.
Nitrogen	1	14	63·6	63·3	62·5	60	1·0	0·97	30·16
Oxygen	1	8	36·4	36·7	37·5	40	0·5	0·55	17·05
<hr/>									
Nitrous oxide	1	22	100·0	100·0	100·0	100	1·0	1·52	47·21

The first column (I.) contains the component elements of nitrous oxide; (II.) shows that 1 atom of nitrous oxide is composed of 1 atom of nitrogen and 1 of oxygen; (III.) shows the equivalent weight of an atom of nitrogen = 14 and an atom of oxygen = 8, producing an atom of nitrous oxide = 22; (IV.) shows the composition *per cent.* calculated from the theoretical equivalents; (V.) (VI.) and (VII.) show the experimental results of the analyses of Davy, Berzelius, and Higgins, and enable us to compare them with the calculated or theoretical composition; (VIII.) shows that 1 volume of nitrogen and half a volume of oxygen, constitute 1 volume of nitrous oxide; (IX.) shows that the specific gravity of nitrogen being 0·97 and half the specific gravity of oxygen being 0·55, the specific gravity of nitrous oxide will be $0·97 + 0·55 = 1·52$; (X.) shows that the weight of 100 cubic inches of nitrogen being 30·16 grains, and of 50 cubic inches oxygen being 17·05 grains, the weight of 100 cubic inches of nitrous oxide will be 47·21 grains.

ROYAL MINT. MAY, 1848.

ERRATA.

- Page 259, line 15, after Gmelin, *insert* as given in column D.
- „ 295, „ 6, *for* nobody, *read* no body.
- „ 309, the maximum of density of water, as stated at page 33, should have been again referred to in this page. The recent experiments of Playfair and Joule (Mem. Chem. Soc. III. 204), place it at 39°·1 Fahrenheit.
- „ 310, line 9, *for* 100 cubical inches weighing, *read* 100 cubical inches of steam weigh.
- „ 406, „ 6, *for* 2 atoms, *read* 1 atom.
- „ 408, „ 31, *for* gas, *read* gases.
- „ 415, „ 5, *for* scruple, *read* sample.
- „ 425, „ 19 from bottom, *for* into composition, *read* into the composition.
- „ 431, „ 20 from bottom, *for* HYDRURURET, *read* HYDRURET.
- „ 468, „ 9 from bottom, *for* Ca O₃, *read* Ca O₂.
- „ 569, „ 20, *for* KI and Zn O + CO₂, *read* KI + Zn O, CO₂.
- „ 573, „ 7 from bottom, *for* hydrogen, *read* nitrogen.
- „ 584, „ 16, *for* product, *read* process.
- „ 584, „ 29, *for* 4S, *read* 4S.
- „ 587, „ 5 from bottom, *for* 2 atoms of nitre and 1 of sulphuric acid, *read* 1 atom of nitre and 2 of sulphuric acid.
- „ 593, „ 21, *for* PEALASH, *read* PEARLASH.
- „ 610, „ 24, *for* effervesce, *read* effloresce.
- „ 612, „ 19 from bottom, *for* anhydrous fluoric, *read* hydrofluoric.
- „ 629, in the table; after boracic, insert acid.
- „ 632, line 19 from bottom, *for* Li, *read* L.
- „ 640, „ 9 from bottom, *for* chlorine, *read* chloride.
- „ 641, „ 11, *for* imbibed, *read* imbued.
- „ 669, „ 7 from bottom, *for* phosphuret of baryta, *read* phosphuret of barium.
- „ 690, line 10 from bottom, *for* NH₄ O, MgO, PO₅, *read* NH₄ O, 2Mg O, PO₅.
- „ 698, „ 17 from bottom, *for* mangnesia, *read* magnesia.
- „ 726, „ 22 from bottom, *for* 2F, *read* 2Fe.
- „ 782, „ 10, *for* HN₄, *read* NH₄.
- „ 831, „ 11, *omit the words* and in nitric acid with the separation of sulphur.
- „ 850, „ 11, *for* 3CO₂ = CO, *read* 3CO₂ + CO.
- „ 873, „ 5 from bottom, *for* 5S₂, *read* 5SO₂.
- „ 977, „ 17, *for* Protochloride, *read* Dichloride.
- „ 1023, „ 16 from bottom, *for* Na O, *read* 2Na O.
- „ 1062, „ 6 from bottom, *for* 2PO₂, *read* 2PtO₂.
- „ 1227, „ 19, *for* xanthoproteic acid, *read* glutine.
- „ 1379, „ 8, *for* C₁₆ H₁₈ O₂₄, *read* C₂₆ H₁₈ O₁₄.

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HISTORICAL SKETCH OF THE PROGRESS

OF

CHEMICAL PHILOSOPHY,

FROM THE TIMES OF THE ALCHEMISTS TO THE COMMENCEMENT OF THE PRESENT CENTURY.

§ I.

CHEMISTRY is that branch of natural knowledge which teaches us the properties of the elementary substances, and of their mutual combinations; it inquires into the laws which affect, and into the powers which preside over their union; it examines the proportions in which they combine, and the modes of separating them when combined; and endeavors to apply such knowledge to the explication of natural phenomena, and to useful purposes in the arts of life*.

Chemistry cannot be said to have existed, as a science, previous to the commencement of the seventeenth century; for although we find, in the writings of the earlier chemists, many curious and important facts and discoveries, these remained useless and unapplied, so long as the minds of men were exclusively directed to the transmutation of the metals, the composition of an universal elixir, and the production of the *Alcahest*, or general solvent. Although, therefore, it may often be amusing, and sometimes profitable, to revert to the crude speculations and waking dreams of the voluminous writers upon these subjects, who were eminent in the fourteenth and two successive centuries, the time of the student will be more usefully occupied in tracing the labors of those who, discarding visionary hypotheses, proceeded to the investigation of truth;

* *Definitions of Chemistry.*—"La Chymie est un art qui enseigne à séparer les différentes substances qui se rencontrent dans un mixte." L'EMERY, *Cours de Chymie*.

"Chemistry is that science which examines the constituent parts of bodies, with reference to their nature, proportions, and method of combination." BERGMAN, *Essay on the Usefulness of Chemistry*.

"Chemistry is the study of the effects of heat and mixture, with a view of discovering their general and subordinate laws, and of improving the useful arts." BLACK, *Lectures*.

"La Chimie est une science qui apprend à connaître l'action intime et réciproque de tous les corps de la nature, les uns sur les autres. Par les mots *action intime*, et *reciproque*, cette science est distinguée de la physique expérimentale, que ne considère que les propriétés extérieures des corps doués d'un volume,

et d'une masse qu'on peut mesurer, tandis que la Chimie ne s'attache qu'aux propriétés intérieures, et n'agit que sur des molécules, dont le volume et la masse ne peuvent pas être soumis aux mesures et aux calculs." FOURCROY, *Système des Connoissances Chimiques*, vol. i., p. 4.

"Die Chemie ist eine Wissenschaft die uns die wechselseitige wirkungen der einfachern Stoffe in der Natur, die zusammensetzung der körper aus ihren und nach ihren verschiedenen verhältnissen, und die Art und Weise kennen lehrt, sie zu trennen, oder sie wieder zu neuen Körperarten zu verbinden." GREN. *Systematisches handbuch der Chemie*, p. 1. Halle, 1794.

"Chemistry is that science which treats of those events or changes in natural bodies, which are not accompanied by sensible motions." THOMSON, *System of Chemistry*, 5th edition, p. 2.

"Most of the substances belonging to our globe are constantly undergoing

and who were led on, not by the vague glimmering of speculative notions, but by the steady daylight of real philosophy*.

It is, I think, among our own countrymen that we discover the fathers of chemical philosophy: for BACON, BOYLE, HOOKE, MAYOW, and NEWTON, present unequivocal claims to that distinctive title. As induction from experiment is exclusively the basis of chemical science, little progress could be made in it till the futility of the ancient philosophical systems had been shown, and their influence annihilated; till the true end of science was rightly defined, and the road to it rendered straight and passable; till the necessity of well-digested experiment had been established, which "first procures the light, then shows the way by its means."

It may seem trite to quote Lord BACON; but, as experience is constantly showing the neglect of the invaluable doctrines inculcated in his

alterations in sensible qualities, and one variety of matter becomes, as it were, transmuted into another. Such changes, whether natural or artificial, whether slowly or rapidly performed, are called chemical; thus the gradual and almost imperceptible decay of the leaves and branches of a fallen tree exposed to the atmosphere, and the rapid combustion of wood in our fires, are both chemical operations.

"The object of chemical philosophy is to ascertain the causes of all phenomena of this kind, and to discover the laws by which they are governed." DAVY, *Elements of Chemical Philosophy*, p. 1.

In the latest editions of Johnson's *Dictionary*, the erroneous and antiquated definition of Boerhaave is very improperly retained. "An art whereby sensible bodies, contained in vessels, or capable of being contained therein, are so changed by means of certain instruments, and principally fire, that their several powers and virtues are thereby discovered, with a view to philosophy or medicine."

The derivation of the word Chemistry can scarcely be said to have been ascertained. The most plausible guesses are the following: from *χυνω*, to melt, or *χυμος*, juice; from *kema*, an oriental word signifying *black*; from *Χημης*, the name of a person eminently skilled in the sciences; from *Chémi*, the Coptic name of Egypt, where the art is supposed to have had its rise.

According to Bryant (*Ancient Mythol.*), it is derived from *chemia*, and that word from *Cham*.

The Rev. Mr. Palmer, Professor of Arabic at Cambridge, has given the following etymology: "Al-chemy, or

more properly Al-kemy, the knowledge of the substance or composition of bodies, so named from the substantive (Kya-mon), that is, the substance or constitution of anything; from the root (Kama.) Golius. *Lexicon*." THOMSON'S *Chemistry*, 5th edit., p. 4, Note.

Conversing upon this subject with my late friend, Dr. Thomas Young, he remarked, that the Egyptians probably neither knew nor cared much about the *composition* of bodies; and that the term Chemistry, as referring to the secret art of transmutation, was probably derived from the Coptic root *hhems* or *chems*, signifying *obscure*, *dark*. The German word *geheim*, *secret*, he said, was perhaps of the same root.

"Hæc ars varia accepit nomina, nam omnium primò dicta fuit τέχνη ποιητική, et antiquis illis temporibus per hanc vocem significabant artem vilia metalla in aurum convertendi, et ejus artifices ποιηταὶ vocari Zozimus dicit. Veteres Ægyptios hanc artem Chimoet vocasse Josephus Scaliger ibi ostendit, sed postea Græci hanc artem χρυσοποιεῖν dixerunt, Arabibus vero, *Alchemia*." BOERHAAVE, *Institutiones Chemiæ*.

* "Tout ce qu'on a dit de l'antique origine de la Chimie, sur les premiers hommes qui ont travaillé les métaux, taillé et poli les pierres dures, fondu les sables, dissous et cristallisé les sels, ne montre à un esprit exact et sévère qu'une vaine et ridicule prétension, semblable à cette par laquelle on voudrait reconnoître les élémens de la géométrie dans l'ouvrage grossier du sauvage qui use les fragmens du rocher, qui leur donne des formes à peu près régulières pour les rendre utiles à ses premiers besoins." FOURCROY, *Discours Préliminaire*.

works, and as students, especially, are too apt to throw off the burden and responsibility of thinking for themselves, by adopting the notions of others, without duly weighing their merit or appreciating their correctness, and often only because they are new, I shall call their attention to one of the many relevant passages of this author:—

“He who would come duly prepared, and fitted to the business of interpretation, must neither be a follower of novelty, custom, nor antiquity; nor indulge himself in a liberty of contradicting; nor servilely follow authority. He must neither be hasty in affirming, nor loose and sceptical in doubting; but raise up particulars to the places assigned them by their degree of evidence and proof. His hope must encourage him to labor, and not to rest; he must not judge of things by their uncommon nature, their difficulty, or their high character; but by their just weight and use. He must, in his own particular, carry on his view with concealment, and yet have a due regard for posterity. He must prudently observe the first entrance of errors into truths, and of truths into errors, without despising or admiring anything. He must understand his own talents and abilities, or the advantages of his own nature. He must comply with the nature of others. He must, as with one eye, survey the natures of things, and have the other turned towards human uses. He must distinctly understand the mixed nature of words, which is extremely capable both of prejudicing and assisting. He must lay it down to himself, that the art of discovering will grow up, and improve, along with discoveries themselves. He must not be vain either in delivering or concealing the knowledge he has acquired, but ingenuous and prudent, and communicate his inventions without pride or ill-nature: and this in a strong and lively manner, well defended against the injuries of time, and fit for the propagation of knowledge, without occasioning errors; and, which is the principal thing of all, it must be such as may select and choose for itself a prepared and suitable reader*.”

The following observations, from the same source, bring us back to our subject:—

“And again; if any one should condescend to regard such things as are accounted rather curious than useful, and take a thorough view of the works of the alchemists, or the followers of natural magic, he might, perhaps, be at a difficulty which he should withhold, his tears, or his laughter. For the alchymist goes on with an eternal hope; and where his matters succeed not, lays the blame upon his own errors; and accuses himself as not having sufficiently understood either the terms of his art, or his author: whence he either hearkens out for traditions and auricular whispers, or else fancies he made some mistake as to the exact quantity of the ingredients, or nicety of the experiment; and thus repeats the operation without end. And if, in the mean time, among all the chances of experiments, he throws any which appear either new or useful, he feeds his mind with these as so many earnest; boasts and extols them above measure; and conceives great hopes of what is behind. It must, indeed, be allowed that the alchymists have made many discoveries, and obliged mankind with useful inventions; but they are well represented in that fable of the old man, who left an estate to his children, buried

* *Prefatory Aphorisms of the Novum Organum Scientiarum.* No. XI.

somewhere or other, he told them, in his vineyard; which they, therefore, fell to dig for with great diligence; whereby, though they found no gold, in substance, yet they received a better vintage for their labor.

“But such as apply to natural magic, and explain everything by sympathies and antipathies, have, by supine and indolent conjectures, placed strange virtues and operations in things; and if, at any time, they have produced works, they are rather suited to admiration and strangeness, than to fruit and advantage*.”

It is my intention, in this introductory chapter, after a brief allusion to the style and views of the alchemical writers, to notice the principal researches of the chemists of the fifteenth and two following centuries; and thus to give an historical sketch of the science, from its early days, to the commencement of the present age.

In reference to the ends and objects of chemical science, under its present aspect, I cannot do better than quote Sir F. W. HERSCHEL, from whose *Discourse on the Study of Natural Philosophy*, I shall be content with the following extract, earnestly advising all students steadily to peruse and consider that excellent and sensible essay:—

“The laws,” he says, “which concern the intimate constitution of bodies, not as respects their *structure* or the manner in which their parts are put together, but as regards their *materials*, or the ingredients of which those parts are composed, form the objects of chemistry. A solid body may be regarded as a fabric, more or less regularly and artificially constructed, in which the materials and the workmanship may be separately considered, and in which, though the latter be ruined and confounded by violence, the former remain unchanged in their nature, though differently arranged. In liquid or aërial bodies, too, though there prevails a less degree of difference in point of structure, and a greater facility of dispersion and dissipation, than in solids, yet an equal diversity of *materials* subsists, giving to them properties differing extremely from each other.

“The inherent activity of matter is proved, not only by the production of motion by the mutual attractions and repulsions of distant or contiguous masses, but by the changes, and apparent transformations, which different substances undergo, in their sensible qualities, by mere mixture. If water be added to water, or salt to salt, the effect is an increase of quantity, but no change of quality. In this case, the mutual action of the particles is entirely mechanical. Again, if a blue powder and a yellow one, each perfectly dry, be mixed and well shaken together, a green powder will be produced: but this is a mere effect arising in the eye, from the intimate mixture of the yellow and blue light separately and independently reflected from the minute particles of each; and the proof is had by examining the mixture with a microscope, when the yellow and blue grains will be seen separate, and each quite unaltered. If the same experiment be tried with colored liquids, which are susceptible of mixing without chemical action, a compound color is likewise produced, but no examination with magnifiers is in that case sufficient to detect the ingredients; the reason obviously being, the excessive minuteness of the parts, and their perfect intermixture, produced by agitating

* *Novum Organum*. Section V.

two liquids together. From the mixture of two powders, extreme patience would enable any one, by picking out with a magnifier grain after grain, to separate the ingredients. But when liquids are mixed, no mechanical separation is any longer practicable; the particles are so minute as to elude all search. Yet this does not hinder us from regarding such a compound as still a mere mixture, and its properties are accordingly intermediate between those of the liquids mixed. But this is far from being the case with all liquids. When a solution of potash, for example, and another of tartaric acid, each perfectly liquid, are mixed together in proper proportions, a great quantity of solid saline substance falls to the bottom of the containing vessel, which is quite different from either potash or tartaric acid, and the liquid from which it subsided offers no indications by its taste, or other sensible qualities, of the ingredients mixed, but of something totally different from either. It is evident that this is a phenomenon widely different from that of mere mixture; there has taken place a great and radical change in the intimate nature of the ingredients, by which a new substance is produced which had no existence before. And it has been produced by the *union* of the ingredients presented to each other; for when examined, it is found that nothing has been *lost*, the weight of the whole mixture being the sum of the weights mixed. Yet the potash and tartaric acid have disappeared entirely, and the weight of the new product is found to be exactly equal to that of the tartaric acid and potash employed, taken together, abating a small portion held in solution in the liquid, which may be obtained, however, by evaporation. They have therefore combined, and adhere to one another with a cohesive force sufficient to form a solid out of a liquid; a force which has thus been called into action by merely presenting them to each other in a state of solution.

“It is the business of chemistry to investigate these, and similar changes; or the reverse of such changes, where a single substance is resolved into two or more others, having different properties from it, and from each other; and to inquire into all the circumstances which can influence them, and either determine, modify, or suspend their accomplishment; whether such influence be exercised by heat or cold, by time and rest, or by agitation, or pressure, or by any of those agents of which we have acquired a knowledge, such as electricity, light, magnetism,” &c.

§ II.

THE transmutation of baser metals into gold and silver, which was the chief, and, in most cases, the only object of the genuine alchemists, was not merely regarded as possible, but believed to have been performed, by some of the more enlightened chemists of the seventeenth century; and in perusing the history of these transmutations, as recorded by HELVETIUS, BOERHAAVE, BOYLE, and other sober-minded men, it would be difficult to resist the evidence adduced, without the aids of modern science. Lord BACON's sound sense has been arraigned for his belief in alchemy, though he, in fact, rather urges the possibility than the probability of transmutation; and, considering the infant state of the experimental sciences, and of chemistry in particular, in his age, and the plausible

exterior of the phenomena that the chemists were able to produce, he is rather to be considered as sceptical than credulous, upon many of the points which he discusses.

HERMES TRISMEGISTUS, who is said to have lived in the year of the world 2076, has generally been quoted as the oldest of the alchemists; there can, however, be very little doubt that the writings attributed to him are entirely spurious. The *Tractatus Aureus*, or *Golden Work*, is evidently a farrago of occult philosophy belonging to a much later period. HERMES, at the outset, is made to apologize for divulging the secrets of the black art. "I should never have revealed them," says he, "had not the fear of eternal judgment, or the hazard of the perdition of my soul, prevailed with me, for such a concealment. It is a debt I am willing to pay to the just, even as the Father of the just liberally bestowed it upon me." After this prelude, we might expect to be let into some of the mysteries of alchemy, but our curiosity is quickly disappointed, by finding that they are only revealed to the eyes and ears of the sons of art; "not to the profane, the unworthy, and the scoffers, who, being as greedy dogs, wolves, and foxes, are not to feed at our divine repast." The reader is then conducted into what is termed the *innermost chamber*, and regaled with a history and explanation of various matters relating to the philosopher's stone, by means of which, "through the permission of the Omnipotent, the greatest disease is cured, and sorrow, distress, evil, and every hurtful thing evaded; by help of which we pass from darkness to light, from a desert and wilderness to a habitation and home, and from straitness and necessities to a large and ample estate." We are then directed to "catch the flying bird," by which is meant quicksilver; "and drown it so that it may fly no more;" this is what is afterwards termed the *fixation* of mercury, by uniting it to gold. It is then to be plunged into the "well of the philosophers," or *aqua regia*, by which its soul will be dissipated, and its corporeal particles united to the "red eagle," or chloride of gold.

GEBER is another great name in the history of alchemy*; the exact period at which he lived is unknown, but it was probably not later than the seventh century. Whatever may be the date or the authenticity ascribed to the works bearing the name of GEBER, they are among the oldest chemical treatises in existence, and merely as such, deserve the perusal of the curious. His three books of alchemy were published at Strasburgh, in 1520, and, if genuine, contain matter that justifies the praise of BOERHAAVE, who considers him as a first-rate philosopher of his age. In his chapter *On the Alchemie of Sol*, after descanting upon the different means of refining and dissolving gold, he describes several *solar*

* "Primus omnium Arabum post Græcos est Geber, cui dant titulum Arabis. Alii dicunt eum fuisse regem, unde *rex Geber Arabs*, dici solet; sed *Leo Africanus*, qui Græcus fuit, et multa descripsit ex antiquis Arabibus, dicit Gebrum illum natione Græcus fuisse, sed derogasse suam religionem, et se dedisse Mahomedæ religioni Arabum, et vixisse septimo sæculo." BOERHAAVE.

Geber was also a physician and astrologer. The following are the principal works on chemistry which have been attributed to him: *De Alchemia*,—*De summa Perfectione Metallorum*,—*De Lapide Philosophico*,—*De inveniendi Arte Auri et Argenti*. These, and some other works bearing his name, whether genuine or not, furnish good specimens of the early alchemical writings.

medicines, in language which is tolerably intelligible; they are all solutions of gold in nitro-muriatic acid, with the addition of quicksilver, nitre, common salt, and some other saline matters. The student is directed to prepare his mind for his pursuits by suitable acts of piety and charity, which, if earnestly and perseveringly carried on, may, after due time, enable him "to change argent vive into an infinite solific and lunific, without the help of anything more than its multiplication."

Alembics, crucibles, and various furnaces, are so fully described, and, if we may believe the MSS., depicted by GEBER, that he deserves to be mentioned also as the inventor of much useful apparatus. Some have asserted his pretensions to the possession of the universal medicine, for he speaks of curing disease; but this seems a mere metaphorical expression, relating to transmutation. "Bring me," says he, "the six lepers, that I may cleanse them;" by which he probably would imply the conversion of silver, mercury, copper, iron, tin, and lead, into gold; these seven metals only having been known at that period. Dr. Johnson supposes that the word *Gibberish*, anciently written *Geberish*, was originally applied to the language of Geber and his tribe.

ARTEPHIUS, in 1130, published several alchemical tracts: we are told by ROGER BACON and others, that he died at the age of 1025, having prolonged his life by the miraculous virtues of his medicines; but his name, and that of JOHN DE RUPESCISSA, are now deservedly forgotten.

The alchemical annals of the thirteenth century are adorned by the name of ROGER BACON, a native of Ilchester, in Somersetshire, and descended from an ancient and honorable family. In 1240, he returned from Paris, and became celebrated among the learned of the University of Oxford. At that time, however, the exposition of ignorance, and attempts to overthrow the dogmas of the schools, was a service of risk and danger; and to this, Friar BACON, for he was a monk of the Franciscan order, laid himself fully open: he was accused of practising witchcraft, thrown into prison, and nearly starved, for exposing the prevalent immorality of the clergy; and, according to some, stood a chance of being burned as a magician.

I know of no work that strikes one with more surprise, than the *Opus Majus* of ROGER BACON; he stands alone like a beacon upon a waste; he is perspicuous and comprehensive; and full of anticipations of the advantages likely to be derived from the mode of investigation insisted upon by his great successor, Chancellor BACON. This resemblance between ROGER BACON, and his illustrious namesake, has scarcely been noticed by the historians of his period; it has, however, not escaped Mr. HALLAM's observation, who adverts to it in his *History of the Middle Ages*. Whether Lord BACON, he says, "ever read the *Opus Majus*, I know not; but it is singular, that his favourite quaint expression, *prærogativæ scientiarum*, should be found in that work; and whoever reads the sixth part of the *Opus Majus*, upon experimental science, must be struck by it as the prototype, in spirit, of the *Novum Organum*. The same sanguine and sometimes rash confidence in the effect of physical discoveries; the same fondness for experiment; the same preference of inductive to abstract reasoning, pervade both works."

The alchemical work of ROGER BACON which has been most prized, is the *Mirror of Alchymy*, but there is little either of interest, or entertainment to be extracted from it*.

ROGER BACON has by some been spoken of as a benefactor to mankind, by others as an enemy to the human race, inasmuch as he is plausibly considered to have invented gunpowder†, an invention by which the personal barbarity of warfare has certainly been diminished, “but which, considered as an instrument of human destruction, by far more powerful than any that skill had devised, or accident presented, before; acquiring, as experience shows us, a more sanguinary dominion in every succeeding age, and borrowing all the progressive resources of science and civilization for the extermination of mankind, appals us,” says HALLAM, “at the future prospects of the species, and makes us feel, perhaps more than in any other instance, a difficulty in reconciling the mysterious dispensation, with the benevolent order of Providence.”

This discovery has sometimes been given to BARTHOLOMEW SCHWARTZ, a German monk, and the date of 1320 annexed to it, a date posterior to that which may be justly claimed for Friar BACON. Upon the authority, however, of an Arabic writer in the Escorial collection, referred to by Mr. HALLAM, there seems little reason to doubt that gunpowder was introduced, through the means of the Saracens, into Europe, before the middle of the fifteenth century, though its use in engines of war was probably more like that of fireworks than artillery. Many authorities might be adduced to prove the common use of gunpowder early in the fourteenth century. EDWARD THE THIRD employed artillery, with memorable effect, at the battle of Cressy; and, in the fifteenth century, hand-cannons and muskets came into use, and gunpowder was in common employ.

ALBERT OF COLOGNE, surnamed THE GREAT, was a contemporary of ROGER BACON; he is celebrated as the inventor of the *brazen head*, which

* Gmelin has given the following list of the chemical writings of Roger Bacon. The two first are given in Mangetus.

1. Speculum Alchymiae.
2. Epistola de Secretis Operibus Artis et Naturæ, et de Nullitate Magiæ.
3. De Mirabili Potestate Artis et Naturæ.
4. Medulla Alchymiae.
5. De Arte Chemiæ.
6. Breviarium Alchymiae.
7. Documenta Alchymiae.
8. De Alchymistorum Artibus.
9. De Secretis.
10. De Rebus Metallicis.
11. De Sculpturis Lapidum.
12. De Philosophorum Lapide.
13. Opus Majus, or Alchymia Major.
14. Breviarium de Dono Dei.
15. Verbum Abbreviatum de Leone Viridi.
16. Secretum Secretorum.

17. Tractatus Trium Verborum.
18. Speculum Secretorum.

† “From saltpetre and other ingredients,” says Roger Bacon, “we are able to form a fire which will burn to any distance.” And again, alluding to its effects, “a small portion of matter about the size of the thumb, *properly disposed*, will make a tremendous sound and coruscation, by which cities and armies might be destroyed.” And again, in the same work, is a passage which, though somewhat enigmatical, is supposed to divulge the secret of this preparation: “Sed tamen salis petræ, *luru mone cap ubre*, et sulphuris, et sic facies tonitrum si scias artificium.” The anagram is convertible into *carbonum pulvere*. Such are the claims of Roger Bacon to a discovery which soon changed the whole art of war.

was demolished by the pious zeal of his pupil, the angelical Dr. AQUINAS*, in consequence of his suspecting it to be an agent of the devil. ALBERTUS MAGNUS was what in our days is termed an universal genius. He is chiefly celebrated as the commentator of ARISTOTLE; but, if we give credit to contemporary writers, he was deeply skilled in all the higher departments of alchemical philosophy. His works, which are very voluminous, were published at Leyden, in 1651, by Peter Jammy. They fill twenty-one folio volumes. Most of his alchemical tracts have been inserted in the *Theatrum Chemicum*.

The names of RAYMOND LULLY of Majorca, and ARNOLD of Villanova†, occur in this page of the history of chemical science. Their merit, however, consists rather in the quantity than quality of their writings. LULLY died on his passage from Africa, in 1315, whither he had been to preach the truths of the Gospel; his body was carried to Majorca, where he was honored as a martyr. BRUCKER says, “he was more ingenious than honest.” His chemical opinions are scarcely worth quotation or abstract. He is said to have converted iron into gold, in the presence of EDWARD THE FIRST, in London, which was coined into rose-nobles‡.

ARNOLD shines as a magician and astrologer. He was a renowned prophet, and predicted that the world would come to an end in the year 1376. He was shipwrecked on the coast of Genoa, in 1313.

ISAAC and JOHN of Holland were also alchemical philosophers of this period§.

About the year 1560, a *Treatise of Alchymy* was published at Paris, attributed to NICHOLAS FLAMMEL. The work, however, is spurious, and was merely ascribed to him from his becoming suddenly, as it is said, very rich. The use he made of his wealth does his memory much credit: he founded hospitals, repaired churches, and endowed several charitable institutions; proceedings which by no means savor of alchemy. Dr. SALMON, who in 1692 published one of the above-mentioned tracts, says, “FLAMMEL was originally a poor scrivener, yet left so great monuments behind him, as must convince the most incredulous that he knew the secret; and performed such mighty works at his own proper cost and charges, as the most opulent prince in Europe can never do the like. I know,” says he, “a gentleman who went to view those mighty buildings and their records. The archives and governors of those places, he told me, own the matter of fact, but deny the means, saying that FLAMMEL was a very pious man, and went a pilgrimage to St. James of Galicia,

* Thomas Aquinas wrote several works on alchemy. “So far as I have perused them,” says Dr. Thomson, “they are exceedingly obscure, and in various places unintelligible. Some of the terms still employed by modern chemists, occur for the first time in his writings. Thus the term *amalgam*, still employed to denote a compound of mercury with another metal, occurs in them. I have not observed it in any earlier author.”

† Raymond Lully was born in Majorca,

in 1236, and Arnold of Villanova in Provence, in 1235.

‡ BERGMAN, *Histor. Chem.*

§ “Sequuntur nunc Johannes et Isaacus Hollandus, pater et filius, qui diffusissimo sermone et magnâ eloquentiâ scripserunt, et si unum vel alterum arcanum exceperis, pulcherrima experimenta fecerunt de sanguine et urinâ humanâ, quæ Helmontius postea, et Boyleus, pro recentioribus inventis habuerunt.”—

BOERHAAVE.

for a reward of which piety, the holy saint bestowed that vast treasure upon him by way of miracle; thereby denying the power of art by which it was certainly effected, to establish a miracle performed by the Romish saint." He was moreover celebrated for his hieroglyphics, of which facsimiles are given in SALMON'S edition. They are much of the same cast as those that now adorn MOORE'S *Almanac*, and quite as edifying.

In SALMON'S collection, we find the *Marrow of Alchymy*, by GEORGE RIPLEY, *Chanon of Bridlington in Yorkshire*, who was a chemist perhaps less deserving of the reputation he acquired, than most of his compeers. He may be quoted as a chemical poet. His *Compound of Alchemie*, dedicated to EDWARD THE FOURTH, is rugged enough, but not unintelligible. The following stanzas from the preface of this piece, given in ASHMOLE'S *Theatrum Chemicum Britannicum*, will afford a fair idea of RIPLEY'S merits as a poet and philosopher:—

But into Chapters thys Treatis I shall devyde,
In number twelve, with dew recapytulatyon;
Superfluous rehearsalls I lay asyde,
Intendyng only to give trew informatyon,
Both of the theoryke and practycall operatyon:
That by my wrytyng who so wyll guyded be,
Of hys intente perfectly speed shall he.

The fyrst chapter shall be of naturall *Calcination*;
The second of *Dyssolution*, secret and phylosophycall;
The third of our elementall *Separation*;
The fourth of *Conjunction* matrimoniall;
The fyth of *Putrefaction* then followe shall:
Of *Congelation* *Albyficative* shall be the sixt,
Then of *Cybation*, the seaventh shall follow next.

The secret of our *Sublymation* the eyght shall show;
The nynth shall be of *Fermentatyon*;
The tenth of our *Exaltation* I trow.
The elevent of our mervelose *Multiplycatyon*,
The twelfth of *Projection*, then *Recapitulatyon*,
And so this treatise shall take an end,
By the help of God, as I entend.

Thus here the Tract of Alchemie doth end;
Which tract was by George Ripley, Chanon, penn'd.

It was composed, writt, and signed his owne,
In anno twice seaven hundred seaventy-one.
Reader, assist him, make it thy desire
That after lyfe he may have gentle fire!—AMEN.

The degree of faith placed in alchemy was of course much shaken by the multiplied experiments which were undertaken during the seventeenth century; in general, however, those who failed, attributed their ill success to any rather than the real cause. SALMON'S creed is that of most of his contemporaries. "As to the great and philosophic work," says he, (meaning transmutation,) "it is my opinion and belief, that there is such a thing in nature. I know the matter of fact to be true, though the way and manner of doing it is as yet hid from me. I have been eye-witness of so much as is able to convince any man endued with rational faculties, that there is a possibility of the transmutation of metals; yet, for all these things, will not advise any man, ignorant of the power of nature and the

way of operation, to attempt the work, lest, erring in the foundation, he should suffer loss, and blame me. Without doubt it is a gift of God from above, and he that attains it must patiently wait the moving of the waters; when the destined angel moves the waters of the pool, then is the time to immerge the leprous metal, and cleanse it from all impurities."

VAN HELMONT says, "I am constrained to believe in the making of gold and silver, though I know many exquisite chemists to have consumed their own and other men's goods, in search of this mystery; and to this day we see these worthy and simple labourers, cunningly deluded by a diabolical crew of gold and silver sucking flies and leeches. But I know that many will contradict this truth; one says it is the work of the devil, and another that the sauce is dearer than the meat."

BERGMAN, in summing up the evidence for and against the possibility and probability of transmutation, and founding his opinion upon the multitude of relations that have been handed down to us by different writers of apparent veracity, one or two of which I shall presently quote, observes that "although most of them are deceptive, and many uncertain, some bear such character and testimony, that, unless we reject all historical evidence, we must allow them entitled to confidence*."

For my own part, the perusal of the histories of transmutation appears to me to furnish solid ground for a diametrically opposite opinion. They are all of a most suspicious character; sometimes the fraud was open and intentional, seconded by juggling dexterity; at other times the performers deceived themselves; they purchased what was termed a *powder of projection*, prepared by the adepts, containing a portion of gold; and when they threw it into the fire with mercury, and found that portion of gold remaining in their crucible, they mistook its source. But the cases which are quoted as least exceptionable, are often exactly those which are really impossible; namely, where the weight of the powder of projection, and of the lead, or other base metal, taken conjointly, was exceeded by that of the gold produced. Such is HIERNES' history of PAYKUL's transmutation, who, with six drachms of lead and one of powder, produced an ingot that was coined into one hundred and forty-seven ducats; and many others. But the most celebrated history of transmutation is that given by HELVETIUS, in his *Brief of the Golden Calf; discovering the rarest Miracle in Nature; how by the smallest portion of the Philosopher's Stone, a great Piece of Common Lead was totally transmuted into the purest transplendent Gold, at the Hague, in 1666*; and, as it is a luminous epitome of all that has been done on this subject, I shall briefly abridge the proceedings:—

"The 27th day of December, 1666, in the afternoon, came a stranger to my house at the Hague, in a plebeick habit, of honest gravity and serious authority, of a mean stature and a little long face, black hair not at all curled, a beardless chin, and about forty-four years (as I guess) of age, and born in North Holland. After salutation, he beseeched me, with great reverence, to pardon his rude accesses, for he was a lover of the Pyrotechnian art, and having read my treatise against the sympathetic powder of Sir KENELM DIGBY, and observed my doubt about the philosophic mystery, induced him to ask me if I really was a disbeliever as to

* *Opuscula*, iv. 127.

the existence of an universal medicine which would cure all diseases, unless the principal parts were perished, or the predestinated time of death come. I replied, I never met with an adept, or saw such a medicine, though I had fervently prayed for it. Then I said, surely you are a learned physician. No, said he, I am a brass-founder, and a lover of chemistry. He then took from his bosom-pouch a neat ivory box, and out of it three ponderous lumps of stone, each about the bigness of a walnut. I greedily saw and handled for a quarter of an hour this most noble substance, the value of which might be somewhere about twenty tons of gold; and having drawn from the owner many rare secrets of its admirable effects, I returned him this treasure of treasures with a most sorrowful mind, humbly beseeching him to bestow a fragment of it upon me in perpetual memory of him, though but the size of a coriander seed. No, no, said he, that is not lawful, though thou wouldst give me as many golden ducats as would fill this room; for it would have particular consequences, and if fire could be burned of fire, I would at this instant rather cast it all into the fiercest flames. He then asked if I had a private chamber whose prospect was from the public street; so I presently conducted him to my best furnished room backwards, which he entered," says HELVETIUS, (in the true spirit of Dutch cleanliness,) "without wiping his shoes, which were full of snow and dirt. I now expected he would bestow some great secret upon me; but in vain. He asked for a piece of gold, and opening his doublet, showed me five pieces of that precious metal which he wore upon a green riband, and which very much excelled mine in flexibility and color, each being the size of a small trencher. I now earnestly again craved a crumb of the stone, and, at last, out of his philosophical commiseration, he gave me a morsel as large as a rape-seed; but I said, this scanty portion will scarcely transmute four grains of lead. Then, said he, deliver it me back: which I did, in hopes of a greater parcel; but he, cutting off half with his nail, said, even this is sufficient for thee. Sir, said I, with a dejected countenance, what means this? And he said, even that will transmute half an ounce of lead. So I gave him great thanks, and said I would try it, and reveal it to no one. He then took his leave, and said he would call again next morning at nine. I then confessed, that while the mass of his medicine was in my hand the day before, I had secretly scraped off a bit with my nail, which I projected on lead, but it caused no transmutation, for the whole flew away in fumes. Friend, said he, thou art more dexterous in committing theft, than in applying medicine; hadst thou wrapt up thy stolen prey in yellow wax, it would have penetrated and transmuted the lead into gold. I then asked if the philosophic work cost much or required long time, for philosophers say that nine or ten months are required for it. He answered, Their writings are only to be understood by the adepts, without whom no student can prepare this magistery. Fling not away, therefore, thy money and goods in hunting out this art, for thou shalt never find it. To which I replied, As thy master showed it thee, so mayest thou perchance discover something thereof to me, who know the rudiments, and therefore it may be easier to add to a foundation, than begin anew. In this art, said he, it is quite otherwise; for unless thou knowest the thing from head to heel, thou canst not break

open the glassy seal of HERMES. But enough; to-morrow, at the ninth hour, I will show thee the manner of projection. But ELIAS never came again; so my wife, who was curious in the art whereof the worthy man had discoursed, teased me to make the experiment with the little spark of bounty the artist had left me; so I melted half an ounce of lead, upon which my wife put in the said medicine; it hissed and bubbled, and in a quarter of an hour the mass of lead was transmuted into fine gold, at which we were exceedingly amazed. I took it to the goldsmith, who judged it most excellent, and willingly offered fifty florins for each ounce." Such is the celebrated history of ELIAS THE ARTIST, and Dr. HELVETIUS.

SIR KENELM DIGBY, whose name is mentioned in this narrative, was a renowned dabbler in the mysterious art. Under the date of seventh November, 1651, in EVELYN's *Diary**, "He gave me," says Mr. EVELYN, "a certain powder, with which he affirmed that he had fixed mercury before the late king. He advised me to try and digest a little better, and gave me a water which he said was only rain water, of the autumnal equinox, exceedingly rectified and very volatile; it had a taste of strong vitriolic, and smelt like aquafortis. He intended it for a dissolvent of calx of gold; but the truth is, Sir KENELM was an arrant mountebank."

The following is another history of transmutation, given by Mangetus (Preface to the *Bibliotheca Chemica Curiosa*), on the authority of M. GROS, a clergyman of Geneva, "of the most unexceptionable character, and at the same time a skilful physician and expert chemist."

"About the year 1650 an unknown Italian came to Geneva, and took lodgings at the sign of the *Green Cross*. After remaining there a day or two, he requested De Luc, the landlord, to procure him a man acquainted with Italian, to accompany him through the town, and point out those things which deserved to be examined. De Luc was acquainted with M. Gros, at that time about twenty years of age, and a student in Geneva, and knowing his proficiency in the Italian language, requested him to accompany the stranger. To this proposition he willingly acceded, and attended the Italian everywhere for the space of a fortnight. The stranger now began to complain of want of money, which alarmed M. Gros not a little, for at that time he was very poor, and he became apprehensive, from the tenor of the stranger's conversation, that he intended to ask the loan of money from him. But instead of this, the Italian asked him if he was acquainted with any goldsmith, whose bellows and other utensils they might be permitted to use, and who would not refuse to supply them with the different articles requisite for a particular process which he wanted to perform. M. Gros named a M. Bureau, to whom the Italian immediately repaired. He readily furnished crucibles, pure tin, quicksilver, and the other things required by the Italian. The goldsmith left his workshop, that the Italian might be under the less restraint, leaving M. Gros, with one of his own workmen, as an attendant. The Italian put a quantity of tin into one crucible, and a quantity of quicksilver into another. The tin was melted in the fire, and the mercury heated. It was then poured into the melted tin, and at the same time a red powder, enclosed in wax, was projected into the amalgam. An agita-

* BRAY'S *Memoirs of John Evelyn*.

tion took place, and a great deal of smoke was exhaled from the crucible; but this speedily subsided, and the whole being poured out, formed six heavy ingots, having the color of gold. The goldsmith was called in by the Italian, and requested to make a rigid examination of the smallest of these ingots. The goldsmith, not content with the touchstone, and the application of aquafortis, exposed the metal on the cupel with lead, and fused it with antimony, but it sustained no loss. He found it possessed of the ductility, and specific gravity of gold; and full of admiration, he exclaimed, that he had never worked before, upon gold so perfectly pure. The Italian made him a present of the smallest ingot as a recompense, and then, accompanied by M. Gros, he repaired to the Mint, where he received from M. Bacuet, the mint-master, a quantity of Spanish gold coin, equal in weight to the ingots which he had brought. To M. Gros he made a present of twenty pieces, on account of the attention that he had paid to him; and, after paying his bill at the inn, he added fifteen pieces more, to serve to entertain M. Gros and M. Bureau for some days, and in the mean time he ordered a supper, that he might, on his return, have the pleasure of supping with these two gentlemen. He went out, but never returned, leaving behind him the greatest regret and admiration. It is needless to add, that M. Gros and M. Bureau continued to enjoy themselves at the inn, till the fifteen pieces, which the stranger had left, were exhausted."

Many of the alchemists have given in detail the processes for the preparation of the Philosopher's Stone; but they are all unsatisfactory, and many of them unintelligible*. The following, which is one of the plainest, is offered as a sample of the general tenor of their proceedings; it is the formula of Carolus Musitanus†.

"1. Prepare a quantity of spirit of wine, so free from water that it is wholly combustile, and so volatile, that when a drop of it is let fall, it evaporates before it reaches the ground; this constitutes the first menstruum.

"2. Take pure mercury, revived in the usual manner from cinnabar; put it into a glass vessel, with common salt and distilled vinegar; agitate violently, and when the vinegar acquires a black color, pour it off and add new vinegar; agitate again, and continue these repeated agitations and additions, till the vinegar ceases to acquire a black color from the mercury: the mercury is now quite pure and very brilliant.

3. "Take, of this mercury, four parts; of sublimed mercury‡ (*mercurii meteorisati*), prepared with your own hands, eight parts; triturate them together in a wooden mortar, with a wooden pestle, till all the grains of running mercury disappear. This process is tedious and rather difficult.

"4. The mixture, thus prepared, is to be put into an aludel, on a sand-bath, and exposed to a subliming heat, which is to be gradually raised till the whole sublimes. Collect the sublimed matter, put it again into the aludel, and sublime a second time; this process must be repeated five times. Thus a very sweet and crystallized sublimate is obtained: it constitutes the salt of wise men (*sal sapientum*), and possesses wonderful properties§.

* See STAHL'S *Fundamenta Chemicæ*,
and JUNKER'S *Conspectus Chemicæ*.

† MANGETI *Bibliotheca Chémica*.

‡ Probably corrosive sublimate.

§ Probably calomel.

“5. Grind it in a wooden mortar, and reduce it to powder; put it into a glass retort, and pour upon it the spirit of wine (No. 1) till it stands about three finger-breadths above the powder; seal the retort hermetically, and expose it to a very gentle heat for seventy-four hours, shaking it several times a day; then distil with a gentle heat, and the spirit of wine will pass over, together with spirit of mercury. Keep this liquid in a well-stopped bottle, lest it should evaporate. More spirit of wine is to be poured upon the residual salt, and after digestion, it must be distilled off as before; and this process must be repeated till the whole salt is dissolved, and distilled over with the spirit of wine. You have now performed a great work. The mercury is now rendered in some measure volatile, and will gradually become fit to receive the tincture of gold and silver. Now return thanks to God, who has hitherto crowned your wonderful work with success; nor is this great work involved in Cimmerian darkness, but clearer than the sun; though preceding writers have imposed upon us with parables, hieroglyphics, fables, and enigmas.

“6. Take this mercurial spirit, which contains our magical steel in its belly, put it into a glass retort, to which a receiver must be well and carefully luted; draw off the spirit by a very gentle heat; there will remain, in the bottom of the retort, the quintessence, or soul of mercury; this is to be sublimed by applying a stronger heat to the retort that it may become volatile; as all the philosophers express themselves,

Si fixum solvas faciesque volare solutum,
Et volucrum figas faciet te vivere tutum.

This is our luna, our fountain, in which the king and queen may bathe. Preserve this precious quintessence of mercury, which is very volatile, in a well-shut vessel for further use.

“7. Let us now proceed to the operation of common gold, which we shall communicate clearly and distinctly, without digression or obscurity; that from vulgar gold we may obtain our philosophical gold, just as from common mercury we obtained, by the preceding processes, philosophical mercury.

“In the name of God, then, take common gold, purified in the usual way by antimony, convert it into small grains, which must be washed with salt and vinegar, till it be quite pure. Take one part of this gold, and pour on it three parts of the quintessence of mercury; as philosophers reckon from seven to ten, so we also reckon our number as philosophical, and we begin with three and one; let them be married together like husband and wife, to produce children of their own kind, and you will see the common gold sink and plainly dissolve. Now the marriage is consummated; now, two things are converted into one: thus, the philosophical sulphur is at hand; as the philosophers say, *the sulphur being dissolved, the stone is at hand*. Take then, in the name of God, our philosophical vessel, in which the king and queen embrace each other as in a bedchamber, and leave it till the water is converted into earth; then peace is concluded between the water and fire; then the elements have no longer anything contrary to each other; because, when the elements are converted into earth, they no longer oppose each other; for in earth

all elements are at rest. For the philosophers say, ‘When you shall have seen the water coagulate itself, think that your knowledge is true, and that your operations are truly philosophical.’ The gold is now no longer common, but ours is philosophical, on account of our processes: at first exceedingly fixed, then exceedingly volatile, and finally exceedingly fixed; and the whole science depends upon the change of the elements. The gold at first was a metal; now it is a sulphur, capable of converting all metals into its own sulphur. Now our tincture is wholly converted into sulphur, which possesses the energy of curing all diseases: this is our universal medicine against all the most deplorable diseases of the human body; therefore, return infinite thanks to Almighty God, for all the good things which he has bestowed upon us.

“In this great work of ours, two modes of fermenting and projecting are wanting, without which the uninitiated will not easily follow our process. The mode of fermenting is as follows: Take, of our sulphur above described, one part, and project it upon three parts of very pure gold, fused in a furnace; in a moment you will see the gold, by the force of the sulphur, converted into a red sulphur of an inferior quality to the first sulphur: take one part of this, and project it upon three parts of fused gold; the whole will be again converted into a sulphur, or a friable mass; mixing one part of this, with three parts of gold, you will have a malleable and extensible metal. If you find it so, well; if not, add other sulphur, and it will again pass into sulphur. Now the sulphur will be sufficiently fermented, or our medicine will be brought into a metallic nature.

“The mode of projecting is this: Take, of the fermented sulphur, one part, and project it upon ten parts of mercury, heated in a crucible, and you will have a perfect metal; if its color is not sufficiently deep, fuse it again, and add more fermented sulphur, and thus it will acquire color. If it becomes frangible, add a sufficient quantity of mercury, and it will be perfect.

“Thus, friend, you have a description of the universal medicine, not only for curing diseases and prolonging life, but also for transmuting all metals into gold. Give therefore thanks to Almighty God, who, taking pity on human calamities, has at last revealed this inestimable treasure, and made it known for the common benefit of all.”

Nearly all the alchemists attributed the power of prolonging life, either to the philosopher’s stone, or to certain preparations of gold; imagining, possibly, that the permanence of that metal might be transferred to the human system. The celebrated DESCARTES is said to have supported such opinions; he told Sir KENELM DIGBY, that although he would not venture to promise immortality, he was certain that life might be lengthened to the period of that of the patriarchs. His plan, however, seems to have been the very rational one of limiting all excess of diet, and enjoining punctual and frugal meals*.

The history of alchemy has been greatly enriched by the labors of the celebrated ELIAS ASHMOLE, who in 1652 published his *Theatrum Chemicum Britannicum*, containing several Poetical Pieces of our famous

* See *Life of Descartes*. CHALMERS’S *Biographical Dictionary*.

English Philosophers, who have written the Hermetique Mysteries in their owne ancient Language.

The most remarkable piece in this collection is the *Ordinall of Alchimy*, by THOMAS NORTON, illustrated by several curious cuts. It treats, in separate chapters, of the objects of the occult science; of the difficulties of attaining them; of the different methods of pursuing them; of the characters of the elements; and of the five concords, of which the first is *Patience*, the second *Assistance*, the third *Instruments*, the fourth *Situation*, and the fifth *Planetary Influence*. It is difficult to select from this production any specimen capable of conveying an idea of its merits, that can come within the limits of a quotation. Perhaps the following lines, picked out of the seventh chapter, touching "the Regiment of Fiers," may serve to convey some idea of the author's talents in the double capacity of poet and philosopher:

In many authors written you may see,
Totum consistit in ignis regimine;
 Wherefore in all things so proceed,
 That heat work no more no less than it need;
 Wherein many of Geber's cooks
 Deceived were, though they be wise in books.
 Such heate wherewith a pig or goose is scalded;
 In this arte *Decoction* it is called;
 Such heate as dryeth lawne karchiefs fair,
 In thirty operations serveth for our ayre!
 But for divisions you must use such heate,
 As cook's make when they roaste raw meate.
Ignis humidus another fier alsoe
 Is, and yet seemeth *oppositum in adjecto*:
 Another fier is fier of desication,
 For matters which be imbibed with humectation.
Ignis corrosdens serveth in this arte,
Elementa propinqua wisely to depart.
 By one point of excess all your work is shent,
 And one point too little is insufficient;
 Who can be sure to find its true degree,
Magister magnus in igne shall he be.
 All that hath pleasure in this booke to reade,
 Pray for my soule, and all both quick and deade.
 In this year of Christ 1477,
 This work was begun, honour to God in heaven.

In later times we have had two or three believers in transmutation. In the year 1782, Dr. PRICE of Guildford, by means of a white and red powder, professed to convert mercury into silver and gold, and is said to have convinced many disbelievers of the possibility of such change; his experiments were to have been repeated before an adequate tribunal, but he put a period to his existence by swallowing laurel-water.

Another true believer in the mysteries of this art was PETER WOULFE, of whom it is to be regretted that no biographical memoir has been preserved. I have picked up a few anecdotes respecting him from two or three friends who were his acquaintance. He occupied chambers in Barnard's Inn, while residing in London, and usually spent the summer in Paris. His rooms, which were extensive, were so filled with furnaces and apparatus, that it was difficult to reach his fire-side. Dr. Babington told me, that he once put down his hat, and never could find it again, such was

the confusion of boxes, packages, and parcels, that lay about the chamber. His breakfast hour was four in the morning; a few of his select friends were occasionally invited to this repast, to whom a secret signal was given by which they gained entrance, knocking a certain number of times at the inner door of his apartment. He had long vainly searched for the elixir, and attributed his repeated failures to the want of due preparation by pious and charitable acts. I understand that some of his apparatus is still extant, upon which are supplications for success, and for the welfare of the adepts. Whenever he wished to break an acquaintance, or felt himself offended, he resented the supposed injury by sending a present to the offender, and never seeing him afterwards. These presents were sometimes of a curious description, and consisted usually of some expensive chemical product or preparation. He had an heroic remedy for illness: when he felt himself seriously indisposed, he took a place in the Edinburgh mail, and, having reached that city, immediately came back in the returning coach to London. A cold, taken on one of these expeditions, terminated in an inflammation of the lungs, of which he died in 1805. He is the author of several papers in the *Philosophical Transactions*. Several pieces of his apparatus, and, among others, an *athanor*, or self-supplying furnace, were given me by Mr. Hatchett, who purchased them of Mr. Woulfe: they are in the Laboratory of the Royal Institution.

A few other persons of less note might be quoted as believers in transmutation, but the history of one is that of all; and, in the emphatic language of Spenser, they were doomed

To lose good days that might be better spent,
To waste long nights in pensive discontent;
To speed to-day, to be put back to-morrow,
To feed on hope, to pine with fear and sorrow;
To fret their souls with crosses and with cares,
To eat their hearts through comfortless despairs:
Unhappy wights! born to disastrous end,
That do their lives in tedious tendance spend.

But although the Alchemists have given us little in the way of useful facts or applicable discoveries, their reign was fruitful in the invention of apparatus. Alembics, stills, retorts, receivers, and a variety of whimsical and complex vessels, in glass and porcelain, are described and depicted in their works; and they not only possessed nearly all the furnaces with which our modern laboratories are necessarily supplied, but were particularly expert in their construction.

§ III.

THERE are many points in alchemical history which have been purposely passed over, as affording nothing worthy of remark, and as suggesting nothing that throws light upon the brighter ages of chemistry. It has been too common to load the alchemists with honors which they ill deserve: the picture of their proceedings, already given, is as correct and faithful as the materials that compose it admit of, and it presents little that the mind rests upon with satisfaction, or reverts to with interest or profit. But there were contemporaries with the alchemists, whose pursuits were conducted upon more rational principles, and whose writings,

though often overshadowed by the clouds of magic and astrology, are, in many instances, illumined by rays of sober experimental investigation; they often indulge in the insane caprices of the mere searchers for the philosopher's stone, but their madness has method in it, and their wanderings are not without a plan.

Of these, the first I shall notice, is BASIL VALENTINE* of Erfurth, who wrote about the middle of the fifteenth century, and who may justly be considered as one of those whose labors contributed to the foundation of modern chemistry: his experiments always had an object, and he details them with intelligible perspicuity. It is true that he often launches into alchemy, but he returns unpolluted by its follies: where he speaks as an adept, he is as absurd as need be; but, as the narrator of experiments, he abounds in shrewd remarks, and was uncommonly successful in his pursuits. The extant works of BASIL VALENTINE are not numerous, and they have mostly become scarce. In 1671 his *Triumphal Chariot of Antimony* was republished at Amsterdam, from the original edition of 1624, with copious notes by Dr. THEODORE KIRKCRINGIUS; and a few years after, an English translation of that celebrated production was printed at London. In 1644 his *Haliographia* appeared at Bologna. This work treats of the preparation, uses, and virtues of mineral, animal, and vegetable salts, and is a curious and well-digested body of information upon a variety of chemical subjects. These are the only works of BASIL VALENTINE that I have been able to meet with, and I believe they contain the pith of his chemical knowledge. In both these works he appears in the double capacity of chemist and physician. In physic he was a brave champion for the chemical sect, and his *Triumphal Chariot of Antimony*, especially, abounds in reflections, not of the mildest description, upon the practice and theories of his adversaries, whom he despises, because, unable to prepare their own medicines; "they know not whether they be hot or cold; moist or dry; black or white; they only know them as written in their books, and seek after nothing but money. Labour is tedious to them, and they commit all to chance; they have no conscience; and coals are outlandish wares with them; they write long scrolls of prescriptions, and the apothecary thumps their medicine in his mortar, and health out of the patient."

But when we find many most important facts recorded in the pages of this writer, we shall readily excuse the irrelevant matter by which they are accompanied; and, in this view, his writings deserve the attentive perusal of those who would trace modern improvements to their parent inventions and discoveries, and these to their more remote and recondite sources. To say nothing of the important preparations of antimony with which BASIL VALENTINE enriched the *Materia Medica*, and of which he has given an intelligible and copious account in the *Currus Triumphalis*, we find, in his works, the first accurate directions for the preparation of nitric, hydrochloric, and sulphuric acids; and were these his only contributions to the laboratory, I need hardly say how richly he merits the eulogies of the moderns, when we reflect upon the numerous uses to which those acids are now applied, upon their importance in several of the most refined and extensive branches of art, and upon the ad-

* Born about the year 1400.

vances in technical and scientific chemistry which have been attained by their aid.

In order to obtain the *water of nitre*, for by that name he designates the acid, VALENTINE directs us to distil three parts of powdered earthenware with one of nitre. The mixture is to be subjected in a proper earthen alembic to a red heat, and a capacious receiver annexed. Now, this process is, in some places, still practised, and, although neither convenient, nor, generally speaking, economical, the acid it affords is sufficiently pure. The opinion of the old chemists, respecting this production of nitric acid, was, that the clay held down the nitre so as to expose it to the searching influence of the fire; but the decomposition chiefly depends upon the attraction of the potassa of the nitre for the ingredients of the clay, a kind of red slag remaining in the retort.

Another mode of procuring nitric acid mentioned by this writer, though probably of more ancient date, since RAYMOND LULLY seems to have known it, comes nearer to the process now in common use, and may, in many situations, be conveniently and economically practised. It consists in distilling equal parts of nitre and green vitriol. The residue consists of sulphate of potassa and oxide of iron; the former may be separated by washing with hot water, and an oxide of iron, of a deep red color, remains, used by the polishers of plate-glass, under the name of *colcothar*.

Under the directions for preparing the *salt of gold* in the *Haliographia*, I find a third mode suggested for the production of acid from nitre, which consists in distilling saltpetre with finely-pounded flints. It depends upon the attraction of silica for potassa, which combine to form a glassy slag, or silicate of potassa.

Such are the facts which are recorded by BASIL VALENTINE respecting the preparation of nitric acid; he termed it *water*, or *acid spirit* of nitre. It was afterwards called *aquafortis*; and its property of dissolving gold, with the addition of sal ammoniac, or of hydrochloric acid, is often adverted to and descanted upon by the same author.

For nearly two hundred years after the discovery of *aquafortis*, its chemical history was but little advanced; nor, indeed, were any facts of importance respecting its true nature made out, until Dr. PRIESTLEY and Mr. CAVENDISH commenced their researches, about the middle of the last century.

But the discovery of nitric acid is certainly second in importance to that of *oil of vitriol*, or, as it is now called, *sulphuric acid*, the honor of which is also due to BASIL VALENTINE; for it is not, as far as my information goes, described in any earlier writer: he frequently mentions it, and the mode of its preparation; and PARACELSUS, and the authors who immediately followed, talk of it as well known, and in common use, though it is probable that it bore a high price, and was but scantily supplied.

In the *Currus Triumphalis*, the *spirit* afforded by the distillation of *vitriol* is not unfrequently adverted to, and its action upon certain antimonial compounds so fully described, as to leave no doubt respecting its nature. In the *Haliographia*, however, *oil of vitriol* is distinctly mentioned; and, what is curious, we find in the chapter of that tract relating to the extraction of the salts of iron, particular directions for the prepara-

tion of *sulphate of iron*, by dissolving iron filings in a mixture of one part of oil of vitriol and two of water: this solution, he says, “when put aside in a cool place, soon forms beautiful crystals;” and in another section we are told, that “this salt is an excellent tonic; that it comforts weak stomachs; and that, externally applied, it is an admirable styptic.” And this, in fact, is nearly all that we can say of the preparation and medical uses of this salt of iron, at the present day.

The mode of obtaining sulphuric acid by the distillation of sulphate of iron, or green vitriol, is still extensively practised upon the Continent, in Germany, Sweden, and more especially at Bleyl, in Bohemia*. The vitriol is first deprived of water of crystallization, and then submitted, in glass retorts coated with clay, to a red heat; white fumes pass over into the receivers, which become very hot during the condensation of these fumes into an unctuous reddish-brown fluid, which, from its viscosity and appearance, acquired the name of *oil of vitriol*: there remains in the vessels a substance of a fine red color, which, when washed and levigated, furnishes the *colcothar*, or *caput mortuum* of vitriol; for the old chemists were in the habit of representing the dregs and last products of substances by the symbol of a death's head and cross-bones.

The oil of vitriol, thus prepared, exhales fumes when exposed to a moist atmosphere, and occasionally congeals or crystallizes; circumstances which led to its name of *glacial oil of vitriol*, and which show that it differs from the acid as ordinarily prepared. It contains, in fact, the anhydrous acid.

That sulphur, during combustion, produces a portion of acid matter, seems to have been known at a very early period; the method of obtaining sulphuric acid by burning a mixture of sulphur and nitre is described by VALENTINE in his *Chariot of Antimony*, under the name of *oil of antimony*, for he employed sulphuret of antimony, as well as sulphur, in its production. The original recipe runs thus:

“Take of antimony, sulphur, salt nitre, of each equal parts, fulminate them under a bell, as oil of sulphur, *per campanam*, is made, which way of preparing hath long since been known to the ancients; but you will have a better way if instead of a bell you take an alembic, and apply to it a recipient; so you will obtain more oil, which will indeed be of the same color as that made of common sulphur, but in powers and virtues not a little more excellent.”

Dr. WARD, the inventor of many celebrated nostrums, was the first person who brought this mode of preparing sulphuric acid into notice in England; he obtained a patent for the invention, and for a considerable time monopolized the manufacture. At length Dr. ROEBUCK, an eminent physician of Birmingham, substituted an apparatus of lead, for the glass vessels previously used. This was in 1746, since which the price of sulphuric acid has been greatly reduced, and the manufacturer consequently enabled to employ it for a variety of purposes, to which it was previously inapplicable, from its scarcity and high price. In 1772, the first manufactory of sulphuric acid near the metropolis was established by Messrs. KINGSCOTE and WALKER, at Battersea†.

* AIKIN'S *Dictionary*, art. Sulphuric Acid.

† PARKES' *Chemical Essays*, vol. ii., p. 388.

I have mentioned that the necessity and advantages of nitre, as an addition to sulphur in increasing the acid product, were known to VALENTINE; but the manner in which it operates, is a later discovery. As the expense of the operation is increased by it, many attempts have been made to supersede its use, by the employment of other materials, under the impression that it merely furnished oxygen; but a little reflection easily proves the fallacy of such a notion; for, even if we burn sulphur in pure oxygen, sulphurous, and not sulphuric acid, is the result. The solution of this chemical problem has been chiefly effected by the researches of MM. CLEMENT and DESORMES, and Sir H. DAVY, who have proved that the products of the nitre are concerned in transferring oxygen to the sulphur. A patent has more lately been taken out for a mode of preparing sulphuric acid by the combustion of pyrites, without the intervention of nitre, but its success is doubtful.

The numerous antimonial preparations described in the *Chariot of Antimony* deserve more notice than they have generally received from the chemical historian; and the perusal of that work affords some insight into the celebrated disputes between the galenical and chemical physicians, which were afterwards pushed so far by PARACELSUS.

BASIL VALENTINE, adverting to the notion that antimony* was poisonous, tells us, that its noxious qualities may not only be subdued by art, but that various properties may be communicated to its different preparations—"As a blacksmith," he says, "with one sort of fire, and iron only is his matter, of which he forms divers instruments. Sometimes he makes a spit, at another time horse-shoes, another time a saw, and at length innumerable other things, every one of which serves for that use for which the smith intended it. So of antimony various works may be made for different uses; in which the artist is the smith that forms, Vulcan is the key which opens, and operation and utility give experience and knowledge of the use. Oh, if foolish and vain men would hear and understand what I write, they would not suck their turbid and insalubrious potions, but hasten to these limpid fountains, and drink of the well of life."

In pursuing his defence of antimony, the author allows its venomous nature, but then tells us, that upon that circumstance its value in medicine depends, upon the principle that venom draws venom to itself; and adduces, as proof of this position, the well-known fact, as he terms it, that a dried toad reduced to powder and sprinkled upon the wound occasioned by a viper's bite, cures it.

§ IV.

PARACELSUS comes next, in chronological order, to his predecessor BASIL VALENTINE, but, as a chemist, he falls far short of that master; his original

* It is probable that the word *Antimony* was first used by Basil Valentine. Tradition relates that having thrown some of it to the hogs, after it had purged them heartily, they immediately fattened; and, therefore, he imagined

that his fellow monks would be the better for a like dose, they having become lean by fasting and mortification. The experiment, however, failed, and they died; whence the medicine was called *Antimoine*.

discoveries are few and unimportant, and his great merit lies in the boldness and assiduity which he displayed in introducing chemical preparations into the *Materia Medica*, and in subduing the prejudices of the galenical physicians against the productions of the laboratory. The principal events of his life are the following: His real name was PHILIP HOCHENER, which he changed, on commencing his professional career, into THEOPHRASTUS BOMBASTUS PARACELsus*. At an early age he visited the most renowned towns in Europe, and, returning to his native country, was made Professor of Medicine and Chemistry at Basle; he availed himself of this public situation, not to instruct the unlearned, but to vilify his contemporaries and predecessors. It is generally said that his dissolute manners and intractable temper obliged him to quit his occupation. But others have told a more plausible story: a rich Canon fell sick, and getting frightened, offered a hundred florins to any one who would cure him. PARACELsus administered three pills, and the Canon got well; but being so soon restored, and by such simple means, he refused to fulfil his promise. The matter was brought before a magistrate, who decreed that the doctor should only recover the customary fee. Irritated at the flimsy excuses and unpardonable ingratitude of the priest, and at the magistrate's partial decision, PARACELsus declared that he would leave the inhabitants of Basle to the eternal destruction which they deserved: he then retired to Strasburgh, and thence into Hungary, where he took to drinking, and died in great poverty at Salzburgh, in 1541, and in the forty-third year of his age. Though we can fix upon no particular discovery on which to found his merits as a chemist, and though his writings are deficient in the acumen and knowledge displayed by several of his contemporaries and immediate successors, especially by THEODORE DE MAYERNE, and DU CHESNE, or, as he was generally called, QUERCITANUS†, it is undeniable that he gave a most important turn to pharmaceutical chemistry; and calomel, first described by CROLLIUS‡ in 1609, with a variety of mercurial and antimonial preparations, as likewise opium, came into general use. Although the chemical physicians, however, were very successful, they were aware of the unpopularity of their means; people were frightened at the idea of mercury and antimony,

* "Hunc virum," says Boerhaave, "alii coluerunt pro Deo; imo, locutus sum cum hominibus qui credunt eum non esse mortuum, sed vivum sedere in sepulchro, pertæsum peccatorum et malorum hominum." The following is an illustrative anecdote of his impudence: "Cum adscenderet Cathedram physico-medicam, sumsit vas æneum cum igne, immisit sulphur et nitrum, et simul Galenum, Avicennam, et Arabes conjecit in ignem, dicens, sic vos ardeditis in gehennâ."

† Du Chesne was a native of Gascony, and physician to Henry the Fourth.

‡ Oswald Crollius was physician to the Prince of Anhalt, and a counsellor of the Emperor Rodolph the Second. His practice and system were opposed

by the celebrated Andrew Libavius, of Halle, who died in 1616. His works were published in 1615, at Frankfort, in 3 vols., folio. Libavius was succeeded by Angelus Sala, of Vicenza, physician to the Duke of Mecklenburgh Schwerin, whose works were published at Frankfort, in 1647, in 1 vol., 4to. The perusal of these authors will be interesting to those who are studying the history of medicine, on account of the important additions which they made to Chemical Pharmacy, and the new substances with which they enriched the *Materia Medica*. They were followers of the doctrines of Paracelsus, but divested their practice of the absurdities in which his tenets were involved.

which were accordingly exhibited under fantastic and assumed names. Towards the end of the fifteenth century, the use of antimony was prohibited at Paris; and BESNIER was expelled the faculty for having persevered in administering it. In England, chemical medicines first began to be extensively employed in the reign of Charles the First. In 1644 SCHRÖDER published his *Chemico-Medical Pharmacopœia*; and shortly after, that of the London College made its appearance; but although the history of pharmaceutical chemistry must not be blended with the abstract progress of the science, yet should it not be forgotten, that the great modern improvements in chemistry have sprung from its applications to medicine, and that the foundations of chemical science are to be found in the medical and pharmaceutical writers of the sixteenth century, who rescued it from the hands of the alchemical pretenders, and gave it a place and character of its own.

The enthusiastic ravings of PARACELSUS, tended to awaken the more solid talents of VAN HELMONT of Brussels, who flourished in the early part of the seventeenth century, and who studied and admired the works of his less modest predecessor. VAN HELMONT has left a curious memoir, containing a sketch of his own life, and exhibiting the various circumstances that gave an impulse to his proceedings, and the different causes that suggested his pursuits. In this biographical relic, there is a vein of sound and unaffected argument, which displays a very amiable turn of mind in the writer. It would, however, be irrelevant to my present subject, to give more than a brief abstract, illustrative of the style and pursuits of the author: "In 1594, being then seventeen years of age, I finished my course of philosophy; but upon seeing none admitted to examinations at Louvain who were not in a gown and hood, as though the garment made the man, I was struck with the mockery of taking degrees in arts. I therefore thought it more profitable seriously and conscientiously to examine myself; and then I perceived that I really knew nothing, or, at least, nothing that was worth knowing. I had, in fact, merely learned to talk and to wrangle, and therefore refused the title of Master of Arts, finding that nothing was sound, nothing true, and unwilling to be declared master of the seven arts, when my conscience told me I knew not one. The Jesuits, who then taught philosophy at Louvain, expounded to me the disquisitions and secrets of magic; but these were empty and unprofitable conceits; and, instead of grain, I reaped stubble. In moral philosophy, when I expected to grasp the quintessence of truth, the empty and swollen bubble snapped in my hands. I then turned my thoughts to medicine, and having seriously read GALEN and HIPPOCRATES, noted all that seemed certain and incontrovertible; but was dismayed, upon revising my notes, when I found that the pains I had bestowed, and the years I had spent, were altogether fruitless; but I learned at least the emptiness of books, and formal discourses, and promises of the schools. I went abroad, and there I found the same sluggishness in study, the same blind obedience to the doctrines of their forefathers, the same deep-rooted ignorance*."

* Johannis Baptistæ Van Helmont | extract is from the *Studia Auctoris*,
Opera omnia. Hafn. 1707. The above | p. 16.

VAN HELMONT was called by his contemporaries, an insane enthusiast; but there is, even in the imperfectly translated and brief quotation which I have taken from the history of his studies, a propitious gleam of that dawn of improvement which was diffused over science by the genius of Lord BACON.

The doctrine of the Chemical Elements was in full vogue during the time of VAN HELMONT, PARACELSUS, and VALENTINE, and salt, sulphur, and mercury, are unequivocally mentioned as the ultimate component parts of almost all the forms of matter. In the writings of VAN HELMONT, there are sundry allusions to the existence of aëriform bodies, and the word *gas*, now in common use, and applied to all aëriform matters differing from atmospheric air, first occurs in his pages: he also distinguishes between condensable gases, or vapors, and incondensable, or permanently elastic fluids; and under the term *gas silvestre*, he seems to comprehend what was afterwards called *fixed air*. As to the general tenor of his writings, it is difficult to separate the chemistry from the miscellaneous matters, and more especially from the medical commentaries with which it is blended; but they abound in hints and observations, which are ingenious and acute. In his experiments on air, he argued very plausibly on its weight and elasticity; and has detailed, with much precision, the effect of temperature and pressure, in his description of the air thermometer.

Entering upon the seventeenth century, the historian of Experimental Science must ever pause to pay a tribute of gratitude and respect to the celebrated FRANCIS BACON; a man whose faults as a statesman, have been eclipsed to the eyes of posterity, by the brilliancy and excellence of his philosophical character.

It may usually be observed, that those who are gifted by nature with superior genius or uncommon capacity, who are destined to reach the meridian of science, or to attain exalted stations in the learned professions, have exhibited early symptoms of future greatness: either indefatigable industry, or extraordinary sagacity, or ardent enthusiasm, have marked their entrance into the affairs of life. At the age of sixteen, BACON was distinguished at Cambridge; and very shortly afterwards, struck with the frivolous subtilty of the tenets of ARISTOTLE, he appears to have turned his mind into that channel which led on to future eminence. The solid foundation of his scientific character, is the *Instauration of the Sciences*. It opens with a general and philosophical survey of the subject; whence he proceeds to infer the futility of the ancient philosophical systems, and to point out Induction, from sober and severe experiment, as the only road to truth. Pursue this, he says, and we shall obtain new powers over nature; we shall perform works as much greater than were supposed practicable by natural magic, as the real actions of a Cæsar surpass the fictitious ones of a hero of romance. Speculative Philosophy he likens to the lark, who brings no returns from his elevated flight; Experimental Philosophy to the falcon, who soars as high, and returns the possessor of his prey. Illustrations of the new method of philosophizing, and the mode of arranging results, conclude this admirable and unrivalled performance.

To do justice to this work, we must, for a moment, forget the present

healthy and vigorous constitution of science, and view it deformed and sickly in the reign of ELIZABETH. We shall then not be surprised at the irrelative observations and credulous details which occasionally blemish this masterly production of the human mind.

But the history of Lord BACON furnishes other materials for reflection. Upon the accession of JAMES THE FIRST, he became successively possessed of the highest honors of the law, and acquired great celebrity as a public speaker and a man of business; yet, amidst the harassing duties of his laborious avocations, he still found time to cultivate and adorn the paths of science, the pursuit of which furnished employment for his scanty leisure, and relaxation in his professional toils; and, when ultimately disgraced, "his genius, yet unbroken, supported itself amidst involved circumstances and a depressed spirit, and shone out in literary productions." Nor should the good feeling of his royal master remain unmentioned, who, after remitting his fine, and releasing him from his prison in the Tower, conferred upon him a large pension, and used every expedient to alleviate the burden of his age, and to blunt the poignancy of his sufferings.

After the death of Lord BACON, which happened in April, 1626, in the sixty-sixth year of his age, the records of science began to assume a brighter aspect; and we discern true knowledge emerging from the dungeons of scholastic controversy, and shaking off the chains of polemical learning.

The middle of the seventeenth century was a period extremely fertile in chemical productions. In taking, however, a comprehensive view of the writers of this age, there are a few only whose labors deserve to be recorded as connected with the advancement of chemical knowledge; that is, as having contributed, by new views and discoveries, to the progress of what may be termed the philosophy of the science. They were generally mere recorders of insulated facts, or publishers of ill-digested and imperfectly arranged catalogues of the various preparations that were used in the arts and in medicine; for the dread with which chemical preparations were viewed by physicians, began now to decline; the *Materia Medica* was filled with new and more convenient forms, and the *Pharmacopœiæ*, published under the authority of different governments, were allowed to divulge the preparation of calomel, emetic tartar, and several other important and useful compounds.

Among the writers of this period there is no one more rich in facts, and original in invention, than GLAUBER of Amsterdam. KUNCKEL was a successful promoter of chemistry applied to the arts: he wrote on the production of phosphorus, and on the art of glass-making, and was a favorite at many courts of Europe, more especially with CHARLES THE ELEVENTH of Sweden, who, in 1693, granted him letters of nobility. In 1673, LEMERY, the elder, conferred much service on chemistry by his dexterity as an experimentalist, and by the plain, perspicuous style in which he publicly taught the rudiments of the science. The discovery of phosphorus belongs also to this period; and although of little interest perhaps in the abstract, it drew a host of inquirers into the precincts of the laboratory, and was productive of more extensive and important consequences than have generally been attributed to it.

Of these writers, there is no one so deserving attention, as GLAUBER : he was not a mere maker of experiments, but he reasoned sensibly, and even acutely, upon their results ; he occasionally oversteps the bounds of modest argument, rudely deprecates the views of his contemporaries, and praises himself beyond all measure ; but this vitiated style was then in fashion, and, unlike most of his contemporaries, he has very sufficient claims to originality of invention. His works were translated into English, and published, as the title runs, “ for public good, by the labour, care, and charge of CHRISTOPHER PACKE, *Phylo-Chemico-Medicus*, in 1689.”

GLAUBER was so laborious an experimentalist, and in his experiments there is so much originality, that it is difficult to select those which can strictly be called discoveries, and upon which his scientific character deserves chiefly to be founded.

The distillation of volatile alkali from bones, and its conversion into sal ammoniac by the addition of spirit of salt ; the preparation of sulphate of ammonia, which he calls *secret sal ammoniac*, and its conversion into common sal ammoniac by distillation with common salt ; the production of blue vitriol by the action of acid of vitriol upon the green rust of copper ; the distillation of vinegar from wood, and the formation of a variety of salts useful in medicine and the arts, by its action upon alkaline, earthy, and metallic substances ; the distillation of muriatic acid, or spirit of salt, from a mixture of common salt and acid of vitriol ; and the extraction of sulphate of soda, or *sal mirabile*, from the residue of that operation, are a few, and only a very few, of the truly important inventions and discoveries that crowd upon us in the perusal of the verbose pages of GLAUBER. Of these, the production of vinegar of wood, and of muriatic acid, may perhaps be regarded as of the greatest interest. The acid liquor produced during the destructive distillation of wood has lately become a manufacture of much importance.

GLAUBER describes the distillatory apparatus, which he calls “ a press for extracting the juice of wood ;” he shows its condensation into an acid liquor ; and directs the method of burning lime, by ranging layers of chalk alternately with those of the wood. He also says, that by rectifying the spirit of wood, “ a sharp hot oil, of a dark reddish color, remains, and the *vinegar* passes over, fit for the preparation of medicines, and all other uses to which common vinegar is applicable.” The oil, he adds, is an admirable preservative of wood, and when saponified with alkali, forms a most valuable manure ; “ a hogshead of which may be carried into fields and vineyards far remote, more easily than ten loads of common manure, which is carried to vineyards in rocky places with great difficulty. As to the spirit, physicians may use this noble and efficacious juice with great honor and profit in the cure of many diseases hitherto incurable ;” and he highly extols the effects of a warm bath, acidulated by the vinegar of wood : he also shows the mode of concentrating it by exposure to cold, when “ the phlegm only freezeth, but the sharp spirit remaineth in the middle of the hogshead, so sharp that it corrodeth metals like aqua fortis.” After many other shrewd and clever remarks respecting the tar of wood, and its acid, GLAUBER closes his discourse, fearing that it will not be believed by many, which, he says, he cannot help ; “ it contenteth me that I have written the truth, and lighted a candle to my neighbours.”

The preparation of muriatic acid, as now commonly conducted, was first devised by GLAUBER; he obtained it by distilling common salt with acid of vitriol, and gives a sufficiently clear account of the nature of the chemical change that ensues. The residue of this operation retains, to this day, the name of *Glauber's salt*; or, as he termed it, *sal mirabile*. Upon its virtues he has descanted at great length, and though, in his history of this salt, its value and uses are preposterously exaggerated, his observations serve to show the diligence and acuteness with which he investigated its applications, and offer proofs of the extensive information which he possessed relative to many processes of agriculture and the arts. Salt, in short, was GLAUBER's favorite element: "It is," says he, "the beginning and the end of all things, and it increaseth and exalteth their powers and virtues: it is the true universal medicine; not that I would have any man persuade himself, that in these words I would assert immortality, for my purpose tendeth not thither, seeing that I am not ignorant there is no medicine against death." And then, adverting to the opposition to chemical medicines by contemporary physicians, he advises them not to envy those "who have received such divine gifts as his wonderful salt, nor to provoke the innocent with their filthy calumnies and slanders, but to leave those things which exceed their capacities. Nothing," he says, "can extinguish truth; it may be prest, but cannot be overcome; like the sun's light, it may be hidden, but not extinguished."

The directions he gives for the preparation of the *sal mirabile*, and the account of its properties, are in general very correct. "Its color ought to be white and transparent: its figure is in long striæ or crystals: its taste is like ice melting upon the tongue, and yields some bitterishness. Being dried in the fire, and all the moisture gone off, it will lose about three parts of its own body, and retain a fourth part only; being dissolved in water, it will recover those three parts again. But, on the contrary, if it shoot into a square figure, and hath as yet a saltish taste, and being dried, loseth but little of its weight, it is not worth a rush, and shows that either the oil of vitriol was not good, or not enough of it used in the operation. These things we would not bury in silence, so that we might well advise young beginners, and withdraw them from their errors."

GLAUBER has great merit as an inventor and improver of chemical apparatus, much of which is depicted in the plates attached to his works. The form of distillatory vessels commonly called Woulfe's apparatus, is found in GLAUBER's *Chemical Furnaces*; and he contrived a very ingenious mode of heating large vessels of water by steam, and with great economy of fuel; a method now often resorted to.

He published a pamphlet, entitled *The Consolation of Navigators, in which is taught how they who travel by Sea may preserve themselves from Hunger and Thirst; and also from those Diseases which are wont to happen in long Voyages. Written for the Health, Comfort, and Solace of all those who travel by Water for the good of their Country*. The sensible plan of employing extract of malt as a portable vegetable diet, and very dilute muriatic acid to quench thirst, is here recommended; and many of the medicinal uses of the muriatic acid are dwelt upon at length, which have been claimed as recent discoveries. GLAUBER was acquainted with meteoric iron, and with the fall of stones. (BRAYLEY. *Annals of*

Philosophy, 1st Ser., xiii. 315.) On the whole, there is no author contemporary with GLAUBER, who has written so much to the purpose, and in whom we find such abundant anticipations of modern scientific improvements. He was cast in the true mould of an experimental chemist, and had he lived in a more propitious age, would probably have rivalled SCHEELE and PRIESTLEY.

§ V.

It is now time to advert to the early proceedings of the ROYAL SOCIETY, as connected with the present subject, a body incorporated by CHARLES THE SECOND in 1662, under a Royal Charter, for the "improvement of natural knowledge." The period of the foundation of this Society was peculiarly favorable to its interests and objects; the country, long distracted by the worst of all evils, a civil war, and afterwards oppressed by the military usurpation of CROMWELL, was threatened, upon the death of the Protector, with the horrors of anarchy, when the restoration of CHARLES THE SECOND healed all divisions, and checked the tide of revolutionary violence. Then was a propitious time to lead the rich and well-informed into the avenues of scientific inquiry, and to substitute the advancement of knowledge for political speculation. Among the first members of the Royal Society are the names of many who were eminent in mathematical and physical knowledge, and of more who afterwards became so; they were vehement in favor of experimental science, which was then in its infancy, and soon acquired vigor by their support; and it is curious to observe among the most active and zealous promoters of these peaceful studies, many who had been famed as party leaders, or actively engaged in political intrigues and revolutionary broils.

The early volumes of the *Philosophical Transactions*, of which the first bears date 1665, consist of small numbers, which were published at irregular intervals, and, from their miscellaneous contents, may be compared to the scientific journals of these days. Exclusive of papers read before the Royal Society, they contain many scraps of literary and scientific value collected by the Secretary, Mr. OLDENBURGH. The publication was continued by Drs. GREW and HOOKE, but the latter discontinued it, probably from the sparing sale; and in 1683 we find Dr. PLOTT resuming the editorship, upon condition that the members would bind themselves to purchase sixty copies of each number. The *Transactions* were periodically published, with some intermissions, however, by the Secretaries of the Society, till the year 1750, when the publication was put into the hands of a Committee of Papers; and since the year 1762 a volume has annually made its appearance*.

In 1666, the Royal Academy of Sciences was instituted at Paris, under the protection of LOUIS THE FOURTEENTH: in its annals the names of HOMBERG, GEOFFROY, and the two LEMERYS, soon became celebrated for their various discoveries and improvements in chemistry. HOMBERG[†], under the auspices of the Regent DUKE of ORLEANS, was an active and successful experimentalist. He discovered the boracic acid, which he prepared under the name of *sedative salt*. He was also the discoverer of *Pyrophorus*. GEOFFROY deserves mention as an active and scientific con-

* THOMSON'S *History of the Royal Society*.

† Born at Batavia, in Java, 1652; died at Paris, 1715.

tributor to Pharmaceutical Chemistry; he was also, I believe, the first compiler of the *Paris Pharmacopœia*.

The early proceedings of the Royal Society of London present many traits of the infant state of experimental science, and not a few absurdities might be selected from among them, the principal of which were lampooned by Sir JOHN HILL, in his *Review of the Works of the Royal Society of London*. This period, however, was adorned with the names of BOYLE* and of HOOKE†; the former a voluminous writer, of a most amiable temper and upright mind; the latter, an original and acute experimentalist, but a peevish and distrustful man‡.

Although BOYLE cannot be said to have fathomed the depths of science, yet his station in life, his mild and prepossessing disposition, his strict honor and integrity, and the unaffected earnestness with which he promoted experimental inquiry, tended to shed a lustre on his pursuits, to elevate their character with the world, and to draw into their precincts many who, without such an example, would have passed their lives in that listless inactivity, then too common with those upon whom fortune smiled; among them Mr. BOYLE made many converts. "It must be confessed," says his contemporary EVELYN, "that he had a marvellous sagacity in finding out many useful and noble experiments. Never did stubborn matter come under his inquisition, but he extorted a confession of all that lay in her most intricate recesses, and what he discovered he has faithfully registered and frankly communicated. In this," says EVELYN, "exceeding my Lord VERULAM, who (though never to be mentioned without honour and admiration) was used to tell all that came to hand. His severer studies did not in the least sour his conversation, and I question whether any man has produced more experiments without dogmatising. He was a corpuscularian without Epicurus; a great and happy analyser, addicted to no particular sect, but, as became a generous and free philosopher, preferring truth above all; in a word, a person of that singular candour and worth, that to draw a just character of him, one must run through all the virtues, as well as through all the sciences§."

* Boyle was born in January, 1627, at Lismore, in the Province of Munster, in Ireland. He was educated at Eton, and afterwards travelled in Italy, Switzerland, and France, and returned to England in 1664. In 1668 he took up his residence in London; and in 1680 was elected President of the Royal Society. He died on the 30th of December, 1691, aged sixty-four.

† Born in the Isle of Wight, 1635; died in London, 1702.

‡ Sir Godfrey Copley, in a letter written about the time of Hooke's death, says, "Dr. Hooke is very crazy; much concerned for fear he should outlive his estate. He hath starved one old woman already, and, I believe, he will endanger himself to save sixpence for anything he wants." In another, written a few weeks after his death, Sir Godfrey

says, "I wonder old Dr. Hooke did not choose rather to leave his 12,000*l.* to continue what he had promoted and studied all the days of his life, I mean mathematical experiments, than to have it go to those whom he never saw nor cared for. It is rare that virtuosos die rich, and it is a pity they should, if they werelikehim." (DR. DUCARREL'S MSS. quoted in *Biog. Dict.*) Hooke sometimes declared that he intended to dispose of his estate for the advancement of natural knowledge, and to promote the ends for which the Royal Society was instituted; to build a handsome edifice for the Society's use, with a library, laboratory, and repository; and to endow a professorship. *Life by WALLER*.

§ BRAY'S *Memoirs of Evelyn*, 2nd edit. 4to., vol. ii., p. 268.

BOYLE died in December, 1691, and his funeral sermon was preached by the celebrated Dr. BURNET, at St. Martin's Church, "in which," says EVELYN, "he spake of his wonderful civility to strangers; the greatest good which he did by his experience in medicine and chemistry; the works, both pious and useful, which he published; the exact life he led, and the happy end he made*."

Upon the whole it may truly be said of BOYLE, that, though he enlightened and adorned the avenues of science, he scarcely enriched it; he wrote much, and generally to the purpose, but he is rather the historian than the actor. It may be remarked, however, that in BOYLE, and especially in his contemporary, HOOKE, we have the first genuine samples of the influence of Lord BACON's doctrines, which actuated all their proceedings, and produced effects marvellously beneficial. Mr. BOYLE's Essays on the successfulness and unsuccessfulness of experiments, and the preface to his philosophical writings, are in the genuine spirit of experimental research; and HOOKE, in the preface to the *Micrographia*, has spoken so much to the point, and in language so novel and bold in the then state of science, that, upon perusing it, we are struck with the entire confidence which it bespeaks for his subsequent experimental details.

After adverting to the deep-rooted errors that have been grafted upon science, by the slipperiness of the memory, the rashness of the understanding, and the narrowness of the senses, and showing that these failings may, in some degree, be obviated by the right ordering and rendering them duly subservient to each other, he proceeds to point out the means of tracing the footsteps of nature, "not," as he says, "in her ordinary course only, but also in her doublings and turnings; and in this investigation, upon which the desirable reform in philosophy is to be founded, there is not so much required any strength of imagination, or exactness of method, or depth of contemplation, as a sincere hand and faithful eye, to examine and record the things themselves as they really appear."

HOOKE then goes on to lament that "the science of nature has been too long made the work of the brain and of the fancy; let it now revert," says he, "to plain and sound observation; and let all intelligence be severely examined; let there be rigour in admitting, strictness in comparing, slowness in debating, and shyness in determining. The understanding is to order all the inferior services of the lower faculties; but yet it is to do this as a lawful master, and not as a tyrant. It must not encroach upon their offices, nor take upon itself the employments which belong to either of them. It must watch the irregularity of the senses, but not go before them, or prevent their information; it must examine, range, and dispose of the bank which is laid up in the memory; but it must be sure to make distinction between the sober and well-collected heap, and the extravagant ideas and mistaken images which there it may sometimes light upon." This is, indeed, the language of Lord BACON, by one who acted as he wrote, for HOOKE was a most diligent experimenter, and has recorded his results with all that cautious sobriety which he advises. "If ever," he says, "I have ventured at small conjectures respecting the causes of the things I have observed, I beseech the reader

* BRAY'S *Memoirs of Evelyn*. *Diary*, vol. ii., p. 30.

to look upon them only as doubtful problems and uncertain guesses, not as unquestionable conclusions, or matters of unconfutable science."

Among the new views and discoveries of HOOKE, connected with chemistry, and many of which are scattered through the writings of BOYLE, there are none of more importance than those relating to the phenomena of combustion, and to the part which the air performs in that process; and as we are now approaching an epoch of our history at which the appearances presented by burning bodies, and the changes which they undergo, were attentively examined and assiduously inquired into, and in which they were considered as one of the main objects of chemical research, it is right that we distinctly understand HOOKE's notions upon this subject, which will be found wonderfully acute, and remarkable for their boldness, as differing from theories then received; and for correctness, as superseding the objections to which the other views are liable.

From the obscure hints in the writings of the Alchemists, and from the more decided language of BASIL VALENTINE, PARACELSUS, and other writers of that cast, it appears that the phenomena of combustion were generally referred to the existence of some subtle and highly volatile principle, which, expanded and agitated by heat, produced flame and fire. When metals were exposed to the action of heat, the greater number were observed to alter their appearance, and, losing metallic brilliancy, became converted into an earth-like residue, to which the name of *Calx* was given. It was generally admitted that, in this process, the particles of the combustible were thrown into violent vibrations, and so transformed into heat and light; and such a supposition was natural enough; for it appears to a superficial observer, unacquainted with the results of modern discovery, that the matter burned is in a great number of cases entirely consumed, and that the principal products are light and heat.

A tract, extremely remarkable for the period at which it was written, appeared on this subject in France about, or previous to, the year 1630. relating to the increase of weight sustained by tin and lead during their calcination. LE BRUN having melted two pounds six ounces of tin, found that in six hours the whole had passed into the state of calx, weighing three pounds one ounce; and, being puzzled at the circumstance, he consulted REY, a physician of Perigord, as to its cause, who immediately set about an investigation of the matter, which terminated, in explicitly referring the cause of the increase, to the fixation of air*.

HOOKE in his investigations, and BOYLE by his experiments with the air-pump, which was now just perfected and coming into use, succeeded not merely in demonstrating the important part performed by the presence of atmospheric air in combustion, but HOOKE carried his inquiries still further, and, in his mind's eye at least, seems to have seen and anticipated the results that were gained at a much later period of chemical science, and established upon less questionable authority.

BOYLE found that a candle, charcoal, sulphur, and some other combustibles, would not burn in the exhausted receiver of his air-pump, which however produced a very imperfect vacuum. When he had pro-

* *Essays de JEAN REY, Docteur en Médecine, sur la Recherche de la Cause pour laquelle l'Etain et le Plomb, augmentent de poids quand on les calcine.* Paris, 1717.

cured a good vacuum, he found that gunpowder would not inflame in it by collision of flint and steel, which he properly attributed to the want of due heat in the sparks resulting from collision; for, on heating the powder in the focus of a lens, it exploded: hence he thought the nitre contained in the gunpowder was concerned in furnishing materials to supply the place of the air*.

HOOKE, in the sixteenth section of the *Micrographia*, relating to charcoal and burned vegetables, observes, that in the ordinary process for making charcoal, the consumption of the wood is prevented by the exclusion of air. The charcoal glows, it is true, but does not burn; hence, he says, may we learn, that the air is the universal dissolvent of inflammable bodies; that this dissolution generates heat, which we call fire, as is the case in many other dissolutions; that this dissolution is made by a substance mixed with the air, that is like unto, or the *very same*, as that which is fixed in saltpetre; that, of the burning body, one portion is turned into air, and another portion is indissoluble; that the dissolving parts of the air are but few, and hence the atmosphere is like those spirits that have much phlegm mixed with them, and become soon glutted; whereas saltpetre abounds more in those solvent particles, and hence a little will dissolve a great sulphureous body quickly and violently; and as other solvents, though but weak, quickly consume the dissoluble body, if the supply be renovated, so air, applied to a shining body by a bellows, will dissolve it as rapidly as saltpetre. From all which he concludes, that there is no such thing as an *element of fire*, but that flame results from the mutual agency of the volatile parts of combustibles, and a part of the atmosphere.

These, although not the very words of HOOKE, but an abridgment of them, contain their unadulterated sense: his expressions show that he had experimented more largely upon the subject, but he was unwilling to extend his account of it till he had completely investigated other parts of the inquiry; he particularly alludes to the use of the air in respiration. I do not, however, find in any of HOOKE's later productions, that he followed up the interesting facts detailed in the *Micrographia*, though in his *Lampas*, published in 1677, he has given a beautiful explanation of the way in which a candle burns: he attributes the light and heat to the action of the air upon the combustible matter of the flame, and shows that the interior of the flame is not luminous, by the simple expedient of viewing its section through a thin piece of glass, or of mica.

The doctrines of HOOKE, concerning the influence of the air in combustion, were further illustrated by JOHN MAYOW†, who, in 1674, published his *Tracts on various Philosophical Subjects*. The date of this work is posterior to that of the *Micrographia*, but anterior to the *Lampas*, and it contains arguments very similar to those promulgated in the former work, without, as far as I have been able to find, any reference to them, or even mention of HOOKE's name. But MAYOW's chemical fame need not be built upon his doctrine of combustion, for he has displayed uncommon talents in various other branches of inquiry.

* New experiments touching the relation betwixt flame and air. BOYLE's *Works*, 4to., London, 1772, p. 563.

† Born in Cornwall, 1645; died in London, 1679.

While these views were promulgated in England, and chemists were busy in endeavouring to raise a theory of combustion, independent of hypotheses, and founded upon experimental inferences only, BECCHER* and STAHL†, in Germany, were at work upon the same subject, and succeeded in establishing an explanation of combustion, which afterwards made much noise abroad, under the name of the *Phlogistic Theory*; and when we revert to the researches whence this theory, as it was called, arose, they carry with them so plausible and accurate an air, and appear so much less at variance with received doctrines, and known facts, that it is not surprising they should have been adopted in preference to the more abstruse, and, as they then appeared, hypothetical explanations, of HOOKE and MAYOW.

BECCHER'S *Physica Subterranea*‡ was published at Franckfort in 1669: I have endeavoured in vain to come at the meaning of much of this publication: but thus far is evident, that he has anticipated the prevailing geological theories of the present day, and has argued upon many terrestrial phenomena, with a degree of plausibility and precision which will bear comparison with the more enlightened and learned views of HUTTON and PLAYFAIR.

His notion of the chemical constitution of bodies amounts to this: the elements of bodies are air, water, and three earths, one of which is inflammable, another mercurial, and another fusible. The three earths, combined with water, constitute an universal acid, which is the basis of all other acids. The combination of two earths produces lapideous bodies; and, in the metals the three earths are united in various proportions. I cannot pretend to explain or elucidate this doctrine, and have no further remark to make upon it, than to request it may be compared with the luminous *experiments* of HOOKE, in order to set the merits of the latter in their true light.

Towards the end of the seventeenth century, the opinions promulgated by STAHL attained universal assent, and of the names of HOOKE and MAYOW nothing was heard for more than half a century.

* Born at Spires, in 1625; died in England, 1685.

† Born in Franconia, 1660; died at Berlin, 1734.

‡ Beccher wrote voluminously upon a great variety of subjects. His principal chemical works are as follows:

1. *Ædipus Chemicus*. 2. *Metallurgia: de generatione, refinatione, et perfectione Metallorum*. 3. *Physica Subterranea*, and its various appendices. 4. *Parnassus Medicinalis Illustratus*. 5. *Laboratorium Portatile*. 6. *Chemischer Rosen-garten*.

Beccher's *Ædipus* is dedicated to Francis Sylvius Deleboë, who, in 1658, was elected the first professor of Medicine in the University of Leyden. He was a man of an acute mind, as appears from his various essays and tracts, more especially from his *Praxeos Med. Idea Nova*. He died at Leyden in 1672.

“Utilissimum profecto munus subiisti, quo tui auditores non verba, sed corpora, non chymerasticos terminos, verum ipsas reales enchyrises, non inanes denique et immateriales facultates, sed a te demonstrati, effectus causas practicas audiunt, vident, tangunt.” Beccher everywhere compliments him as a man not of words, but of deeds; as a philosopher, who eminently sought to render science popular and intelligible to all capacities.

The language of Beccher's *Physica Subterranea* is sufficiently inelegant and incorrect. “Excuso Latinitatem in hoc opere,” says he, “quam barbaram esse fateor, ob materiem et ob scriptionem, in specie scriptionis modum: ex ore enim dictantis totum opus conceptum est. Sic rebus attentus, verba neglexi.” This is at once an example and apology.

Rejecting the mercurial earth of BECCHER, STAHL retained as elements, water, acid, earth, and fire, or, as he termed it, *Phlogiston*, a principle of extreme tenuity, and prone to a kind of vertiginous motion in which it appears as *fire*. He went beyond BECCHER in adducing experimental proofs of his hypothesis. When phosphorus is burned, it produces an acid matter, with the evolution of much heat and light; consequently, phosphorus consists of acid and phlogiston: if this acid be now heated with *charcoal*, or other body abounding in phlogiston, phosphorus will be re-produced.

When zinc is heated to redness, it burns with a brilliant flame, and is converted into a white earthy substance, or calx. Hence zinc consists of this earth and phlogiston.

Now, it will be observed, that nothing is said here of the *increase of weight* which REY attributed to the condensation of air, and which MAYOW has as distinctly referred to the fixation of HOOKE's nitro-aërial particles. Nor is that obstacle taken into the account which BOYLE's experiments had suggested, and which HOOKE is particularly fond of dwelling upon, namely, that *bodies will not burn without air*.

However, this hypothesis of STAHL, notwithstanding the increase of weight in the burning body, the requisite presence of air, and other bars against it, was immediately embraced by the generality of chemists, and maintained an unimpeached dominion for upwards of fifty years, until shaken and upset by the arguments of LAVOISIER, who, availing himself of the discoveries of SCHEELE, PRIESTLEY, and BLACK, brought an insuperable mass of evidence to bear against the doctrine of phlogiston*.

That constituent of the air which HOOKE had detected in nitre, and which MAYOW called its *nitro-aërial particles*, was, under the new title of *oxygen*, regarded as accessory to all cases of combustion. It was presumed that this aërial matter consisted of heat and light, combined with a ponderable base, which united with the combustible, conferring upon it new characters, while the other elements were extricated under the form of fire. But to this explanation two difficulties soon presented themselves; the one, that in many cases of combustion, aëriiform matter, instead of being absorbed and decomposed, is evolved and composed; and the other, that the evolution of heat and light is not proportional to the volume of air condensed, but depends upon the rapidity of the condensation, and upon the nature of the combustible. These objections, however, cannot be fully discussed without a reference to the doctrines of heat, light, and electricity, which must not now be entered upon.

* Stahl's doctrines are very ably set forth in his *Three Hundred Experiments*, published at Berlin in 1731; and in his *Fundamenta Chemiæ*, Nuremberg, 1723 and 1732. He noticed the necessity of air to combustion, but he considered flame or fire as resulting from its violent ethereal agitations. Stahl is continually urging circumspection in hypotheses, yet preconceived opinions are always leading him to erroneous

conclusions, as the following passages amply prove. "Aer ignis est anima, hinc, sine aere nihil potest accendi vel inflammari."—"Aer in motum excitatus, seu ventus artificialis, vel etiam naturalis, mirum excitat motum ætheris, seu flammam; hinc ad ignem fusorium, et vitrificatorium, promovendum follibus opus est; imo gradus et vehementia ignis dependet multum ex aeris admissione."—*Fund. Chem. dogmat. et ration.*, p. 22.

§ VI.

MAYOW, whose name was mentioned in the last section coupled with that of HOOKE, in researches concerning the influence of air upon combustion, is the first writer who divulged views worth recording upon the subject of respiration, and who has elsewhere displayed some shrewd guesses concerning the causes and effects of chemical affinity. In the first case, he opened a communication between chemistry and physiology; and, in the latter, he extricated a most important and fundamental branch of chemical philosophy, from the mire of false reasoning, and planted it in the precincts of experimental research.

MAYOW was the ornament of his time and country as an experimental inquirer; but, unfortunately, he seems to have fallen upon unpropitious ground, and his talents, instead of having been awakened by emulation, were damped by the coldest reception. He was a native of Cornwall, and died at the early age of thirty-five, at the house of an apothecary in York-street, Covent-garden. Dr. BEDDOES, and more lately, Dr. YEATS*, have each asserted his claims to several of the discoveries attributed to modern experimenters, and they have in many points made out an irresistible case in his favor.

At an early period of his experiments, MAYOW seems to have been struck with the analogy between the phenomena of combustion, and those of respiration, and although many of his conclusions are full of error, there are more which are correct and even refined. He burned a candle under a bell-glass, and found the air so deteriorated as to be unfit for the continuance of combustion. He then confined a mouse in a similar portion of air, and it soon manifested the want of its renewal. Then, by putting a mouse and a candle under the same bell-glass, he found it live only half the time that it had survived when under the glass alone. He then reversed the experiment, and endeavoured to fire combustible matter in air that had been spoiled by breathing; and finding that it would not burn, he observes, that “the nitro-aërial particles are absorbed both by the candle and the animal†.”

Examining the residuary air standing over water after combustion, he found that it was a little lighter than the atmosphere, and extinguished flame; thus remarkably describing nitrogen by its principal properties, namely, that it does not support combustion, that it is not absorbed by water, and that its specific gravity is inferior to that of atmospheric air.

When MAYOW speaks of the *destruction of the elasticity* of a portion of the air, he alludes to its absorption by water; and finding the carbonic acid, formed by respiration and combustion, to be thus absorbed, and its formation always connected with the loss of power to support flame, or of its nitro-aërial parts, he talks of restoration of elasticity by restoring the nitro-aërial matter.

MAYOW also obtained *hydrogen gas* by acting upon iron by dilute

* *Observations on the Claims of the Moderns to some Discoveries in Chemistry, &c.* By G. D. YEATS, M.D., London, 1798.

† See the 1st and 2d Tracts, *De Sal-nitro, et Spirito Nitro-aërio*, and *De Respiratione*.

sulphuric acid; and *nitrous gas*, by immersing the same metal in dilute *aquafortis*. Upon the whole, MAYOW's experiments upon respiration, and upon the gases, are something more than ingenious. Considering the novelty of the subject, and the imperfection of his apparatus, they may be considered as surprising efforts of experimental diligence; and his conclusions may be ranked as remarkable indications of a fruitful mind, not wandering amongst hypotheses, but settling upon the results of experiment.

Not satisfied with having ascertained that one part only of the atmosphere supports life, he extended his inquiry to the subsequent influence of that part upon the system. It was the prevailing notion of his time, that respiration cooled the blood; but having observed in the nitro-aërial, or fire-air particles, an essential to flame and fire, he considered their absorption as necessarily connected with the heat of the blood; he observed an analogy between the respiration of animals and that of plants; and to show the existence of air in the blood, he had recourse to the air-pump, which, he says, extricates it more copiously from arterial than from venous blood.

The most remarkable Chapter, however, of MAYOW's tract, is that relating to the "mutual action of salts of contrary kinds," or, in other words, to chemical combination and decomposition, a subject which he has handled in so masterly a manner, and which is so ably supported by experiments, that, although anticipated in respect to his researches on the air, by HOOKE, we must here give him due credit as an original inquirer.

It was imagined by those predecessors of MAYOW who expounded their notions respecting chemical affinity, that bodies combined in consequence of certain mechanical forms of their particles; and that when an acid was added to an alkali, the salt produced was a perfectly new product, resulting from the *annihilation* of the particles of its components. It was not admitted, or at least not generally admitted, that the acid and alkali existed as such, and might again be separated from the neutral salt. MAYOW first set about rectifying this gross error. When spirit of salt, he says, is mixed with *sal volatile*, sal ammoniac is produced, in which, it is true, neither the properties of acid, nor of alkali, are apparent; yet, if salt of tartar be distilled with sal ammoniac, the volatile alkali will be displaced, with all its previous characters, because there is a greater attraction between spirit of salt and tartar than between spirit of salt and volatile alkali. Again, to show that the acid is not destroyed in saline combinations, he instances the decomposition of nitre by oil of vitriol, which, he says, displaces the nitric acid, and the residuum in the retort furnishes vitriolated tartar. It may be asked, he says, why, when nitre is heated, the nitric acid does not rise, for it is, as we have just seen, very volatile: the reason is, that it is restrained and kept down by its attraction for the tartar, and can only be displaced by bodies which have a stronger attraction for tartar than it. This is excellent reasoning, and it would be difficult, with all the advantages of modern acquisitions, to adduce two more illustrative cases than those which MAYOW has furnished. He then goes on to show that acids have a greater attraction for alkalis than for metals. The metals, he says, are soluble in one or other of the acids, but their solutions are decomposed by salt of tartar; the acid then combines with the tartar, and the metal is precipitated. In the same way

alkali unites to sulphur; but if this combination be dissolved in water, and acid added to the solution, the sulphur falls, and the acid and alkali unite. Combinations of the metals with sulphur are also decomposed by acids; thus, if sulphuret of antimony be distilled with aquafortis, the acid and metal combine, and sulphur sublimes.

Having given other similar instances of the combination of sulphur with metals and alkalies, he proceeds to some general views connected with the subject, among which the following deserve particular notice. Although, he says, sulphur enters into these combinations, we are not to imagine, as some have done, that sulphur includes an acid, and thence derives its powers of combination, in consequence of its containing an opposite nature; on the other hand, it is clear, he adds, that the combination is independent of any such hidden cause, and is the mere result of the mutual affinity of the substances. He then cautions those concerned in the compounding of medicines, to beware of the new compounds that may result in consequence of these mutual attractions and decompositions, for "one substance may destroy the efficacy of another, and something perfectly different from the original may result." It is curious, he remarks, that when acid of vitriol is poured upon salt of tartar, so as to form vitriolated tartar, a great effervescence ensues; but if the acid be previously combined with a metal, this is not observed, and yet vitriolated tartar is equally formed; as when salt of tartar is added to solution of green vitriol. In these cases, he says, the acid part of the salt of tartar is retained by the metal; thus giving an explicit account of a frequently occurring case of double decomposition.

These views, relating to chemical attraction, are at once clever and correct, and their merit will be especially enhanced by a comparison with the absurd and groundless speculations previously entertained upon this subject. But MAYOW has other and more weighty evidence in his favor, for it is remarkable that his views and language were adopted by NEWTON, and that the sketch of a theory of chemical attraction given by that philosopher in the Queries annexed to the third book of Optics, is nearly in the language, and quite in the spirit and meaning, of his predecessor MAYOW. The following are a few of the points urged by NEWTON in the explication of these phenomena:—

If carbonate of potash be exposed to air it deliquesces, in consequence, says NEWTON, of an attraction between the salt and the particles of water contained in the atmosphere. And why does not common salt and saltpetre deliquesce in the same way, except for want of such attraction?

And again, where he especially comes in contact with MAYOW, he says, when spirit of vitriol, poured upon common salt or saltpetre, makes an ebullition, and affords on distillation the muriatic and nitric acids, the acid part of the spirit of vitriol staying behind, does not this argue that the fixed alkali in the common salt and saltpetre, attracts the acid spirit of the vitriol more strongly than its own spirit, and not being able to hold them both, lets go its own? How these attractions may be performed, continues NEWTON, I do not here consider; what I call *attraction* may be performed by impulse, or by some other means unknown to me: I use that word to signify any force by which bodies tend towards one another, whatever be the cause. Thus, he says, muriatic acid unites to

salt of tartar, by virtue of their respective attractions; but when oil of vitriol is poured upon this compound, the former acid is displaced by the superior attraction of the latter. Silver is separated from aquafortis by quicksilver; quicksilver by copper; and copper by iron; which argues that the acid particles of the aquafortis are attracted more strongly by iron than by copper; by copper than by quicksilver; and by quicksilver than by silver*. Thus, then, chiefly by the experimental labors of MAYOW, and the sagacious views of NEWTON, the old and prevailing notions of the atomic forms of bodies, the hypothesis of hooks, rings, points, and wedges, by which the component parts of bodies were supposed to be held united, gave way to a simple and independent expression of facts.

It has often been said, that anticipations of modern discoveries which could alone be demonstrated by the progress of experimental research, are characteristic of the writings of NEWTON, and proofs of his sagacity and penetration: he inferred that the diamond consisted of inflammable matter, and suspected the existence of a combustible element in water, very long before either of those subjects had been experimentally investigated; and in his notions relating to the subject of chemical attraction, he has an anticipation not less striking, relating to the connexion between chemical and electrical attraction. "The attractions of gravity, magnetism, and electricity, reach to very sensible distances, and so have been observed by vulgar eyes; and there may be others which reach to so small distances as hitherto to escape observation, and perhaps electrical attraction may reach to such small distances without being excited by friction†."

I shall conclude this subject with some account of the progress more lately made in elucidating the doctrines of chemical attraction.

In 1718, GEOFFROY‡ invented those tables of affinity which are now often given in elementary works, and which have proved of service in extending chemical knowledge. He considered the order in which bodies separate each other from a given body, as constant. Thus, he thought the metals were always separated from acids by the absorbent earths, these by volatile alkali, and the volatile by the fixed alkalis; to represent, therefore, the attraction of acids for these substances, he placed them at the head of a column, with the other bodies beneath, in the order of attraction, as shown in the margin.

He then constructed a column for each particular acid; thus the table for nitric acid taken from NEWTON'S experiments would stand as annexed:—

GELLERT, and LIMBOURG, in 1751 and 1758, extended, and, in some respects, improved these tabular representations of the results of attraction; but no considerable progress was made in the investigations connected with the subject, until BERGMAN published his dissertation upon it in 1775.

ACIDS.

Fixed alkalis.
Volatile alkali.
Absorbent earths.
Metals.

NITRIC ACID.

Fixed alkali.
Volatile alkali.
Earths.
Iron.
Copper.
Lead.
Mercury.
Silver.

* NEWTON'S *Optics*, book iii., query 31.

† *Optics*, book iii.
‡ *Mem.*, Paris, 1718.

Of BERGMAN'S character and merits as a chemist, I shall speak afterwards, confining myself at present to the views which he entertained upon the subject of affinity, or, as he called it, *elective attraction**.

BERGMAN considered that every substance possessed a peculiar attractive force for every other substance with which it combines; a force capable of being represented numerically: he regarded decomposition as complete; that is, whenever a third body *c*, is added to a compound *a, b*, for one of the constituents of which it has a stronger attraction than that which already exists between them, the compound will be decomposed, and the whole of one of its elements transferred to the added body. Thus, suppose the attraction of *a* for *b* to be represented by 1, and of *a* for *c* by 2, then the addition of *c* to *a b* will produce the compound *a c*, and *b* will be separated. When lime-water is added to nitrate of magnesia, the latter earth is precipitated, and the former combines with the nitric acid. Hence, nitric acid poured upon a mixture of lime and magnesia, dissolves the former, in preference to the latter earth.

The observation of these facts led BERGMAN to call this kind of attraction *elective*, and he has given tables, showing these relative attractions of bodies in the dry and humid way. Thus:

BERGMAN'S opinions relating to affinity were generally admitted as correct, till BERTHOLLET published his work on *Chemical Statics* in 1803, in which he endeavoured

SILVER.	OXIDE OF SILVER.
—	—
Lead.	Sulphuric acid.
Copper.	Oxalic do.
Mercury.	Phosphoric do.
Bismuth.	Nitric do.
Tin.	Tartaric do.
Gold.	Citric do.

to revive, under a new aspect, some of the old chemico-mechanical doctrines, and to prove that the forms of the acting particles, and their magnitudes, or masses of matter, were concerned in influencing the results. Though these doctrines may now be considered as disproved, they had many advocates, and were gaining ground, until the promulgation of the so-called *atomic theory*. The experiments adduced by BERTHOLLET in support of his hypothesis, appeared at first very satisfactory; but upon minute inspection they have their weak points, and many of the errors into which they led have been successfully unravelled, by Professor PFAFF, of Kiel, by Sir H. DAVY, and others. In illustration of the agency of the mass of matter, BERTHOLLET has adduced the mutual action of sulphate of potassa and baryta: when solution of baryta is added to sulphate of potassa, potassa is liberated, and sulphate of baryta is formed, and precipitated insoluble; but if a large quantity of potassa be added to a small quantity of sulphate of baryta, the mass will, according to BERTHOLLET, prevail over what appears to be the real chemical affinity, and sulphate of potassa will be formed, and baryta evolved. But Sir H. DAVY pointed out the fallacy to which this experiment is liable, by showing that pure potassa does not effect any change upon sulphate of baryta, but that, making the experiment in open vessels, part of the potassa acquires carbonic acid, and then a double affinity is brought into action, the bodies present being carbonate of potassa and sulphate of baryta†.

* *De Attractionibus Electivis. Opus-*
cula, vol. iii., p. 291.

† *Elements of Chem. Philos.*, p. 119.

BERTHOLLET's notion, that the acting bodies are divided among each other, in proportions depending upon their relative masses and attractions, has been combated and disproved by PFAFF*, who has shown that tartrate of lime is completely decomposed, by adding to it a quantity of sulphuric acid, exactly sufficient to saturate the lime it contains; and in the same way he has shown that oxalate of lead is decomposed, by adding sulphuric acid sufficient to saturate the oxide of lead.

But the establishment of the Atomic Theory, from which we learn that bodies combine only in certain definite proportions, has gone further to elucidate the important subject of chemical attraction, and to subvert former doctrines, than any previous objections or partial experimental investigations. In establishing this theory, all the eminent chemists of Europe have taken an active part. Its foundation was apparently laid by Mr. William Higgins, of Dublin, previous to the year 1789; for the essential facts, which have subsequently been followed up, and worked out by later chemists, are to be found in his *Comparative View of the Phlogistic and Antiphlogistic Theories*. In the year 1814, he published his *Experiments and Observations on the Atomic Theory*, to which I may also refer the historical reader.

Between the years 1792 and 1802, Dr. RICHTER, of Berlin, published his *Geometry of the Chemical Elements*†, containing a series of tables, showing the weight of each base, capable of saturating one hundred parts of each acid; and the weight of each acid, capable of saturating one hundred of each base. He observed, that in all these tables, the bases and the acids followed the same order; and further, that the numbers in each table constitute a series having the same ratio to each other in all the tables. Thus, supposing in the table of sulphates, one hundred parts of acid were saturated by one hundred of soda, two hundred of potassa, and three hundred of baryta; then in the table of nitrates the same ratio would hold good, and the soda, potassa, and baryta would there also stand to each other in the relation of one, two, and three.

Thus was explained why, when two neutral salts decomposed each other, the newly formed salts are also neutral; for the same *proportion* of bases that saturate a given weight of one acid, saturate a given weight also of all the other acids. Hence numbers may be attached to each acid and to each base, indicating the weight of it which will saturate the numbers attached to all the other acids and bases. Upon this principle, elementary works on chemistry contain tables of the equivalent numbers, or atomic weights of bodies; and upon the same principle, Dr. WOLLASTON, by adapting such table of numbers to a moveable scale, on the principle of GUNTER's sliding rule, has constructed the *logometric scale of chemical equivalents*, which is so important and valuable an instrument to the practical chemist.

I cannot enter into further details respecting the researches which have established and elucidated this highly important subject, without entering into discussions involving the labors of contemporary chemists; and must, therefore, here merely refer to the investigations of Dalton‡

* *Annales de Chimie*. LXXVII.

| *Messkunst Chemischer Elemente*.

† *Anfangsgründe der Stöchiometrie, oder*

| ‡ *New System of Chemical Philosophy*.

and Gay Lussac* connected with it, and to the details which will be found in another part of this work.

§ VII.

BEFORE we proceed with the regular thread of our historical sketch, which is now carrying us into that eventful period for chemistry, and indeed for the progress of all the sciences, the first half of the eighteenth century, it is requisite rapidly to review some collateral investigations which occupied the philosophers of the seventeenth century, and which, though not strictly chemical, contributed much to the progress and perfection of some of the more difficult and abstruse branches of that department of knowledge.

Of these inquiries, it will especially be right to notice such as relate to the phenomena and effects of *heat*, which, in consequence chiefly of the invention of the *thermometer*, were pursued with a degree of ardor and success, highly creditable to the diligence and sagacity of the individuals concerned. Among them, BOYLE is entitled to particular praise; and though his inquiries are blended with much irrelevant and miscellaneous digression, they contain materials amply important and interesting; materials which paved the way for some of the most eminent achievements in chemical science.

It has been disputed to whom the honor of inventing the thermometer belongs; some have given it to CORNELIUS DREBBEL†, and some, with more plausibility, to SANTORIO‡ of Padua. But, when we reflect upon the imperfection and comparative uselessness of the instruments attributed to those claimants, and when the construction of the thermometer now in use may be indisputably referred to the Florentine Academicians, the disputes respecting priority become of little importance. Air was first used as a means of exhibiting, by its expansion and contraction, the alternations of heat and cold; and VAN HELMONT has described, with some minuteness, several modifications of the *air thermometer*§. But however valuable such thermometers may be for particular purposes, they are rendered extremely inconvenient by the rapid and great dilatability of air by moderate changes of temperature: besides which, it is very difficult so to construct air thermometers as to agree among themselves in indicating the same degree, when applied to bodies of similar temperature. The Academicians del Cimento were the first to employ thermometers constructed as we now see them. They used tubes, with a bulb containing spirit of wine, and closed so as to exclude the influence of air, and prevent the evaporation of the liquid. This thermometer, however, though much superior to, and more useful than the old air thermometer, was yet an useless instrument, if we speak of it comparatively with those now constructed; for, there being no fixed point at either extremity of the scale, the graduation was arbitrary, and no two instruments, when placed in an atmosphere of the same temperature, indicated the same degree of heat.

* *Mémoires d'Arcueil*, ii. 287.

† Born in Holland, 1572; died in London, 1634. He is also said to have invented the microscope.

‡ Born at Capo d'Istria, 1561; died at Venice, 1636.

§ *Opera Omnia*, Art. Aër, p. 61.

There is some confusion in this part of the history of the thermometer, for, though the Florentine Academicians state that their scale generally commenced at the temperature of freezing, they represent that point by various terms or degrees, unsusceptible of comparison, and say nothing of the differing temperature of ice, which may exist at 32° , or any inferior degree. In Italy, however, it is most probable that the ice was in a thawing state, and therefore about 32° of FAHRENHEIT'S scale; but all registers of the weather, and all enumerations of high and low temperatures, are quite unintelligible, as recorded by the experimentalists of that period.

"The great and truly honourable Mr. BOYLE" turned his mind with much earnestness to the construction of a *scale* for thermometers, and seems to have had it in contemplation to set out with the temperature at which water *begins* to freeze; "but the objections which he apprehended might be made to this method scared him so much," says Dr. MARTINE*, "that he prosecuted no further this consideration of fixing a standard for making and graduating thermometers all in the same way." Dr. HALLEY† observed, that the same thermometer always indicated the same temperature, in places deep under ground, where neither the heat of summer nor the cold of winter seemed to produce any effect; and MARRIOTTE and DE LA HIRE had made the same remark upon thermometers placed in the caves of the observatory at Paris. But Dr. MARTINE, whose authority is, in most respects, very exact, gives Dr. HALLEY the merit of fixing upon the boiling-point of water as a standard of graduation, which elevates the quicksilver in the thermometer tube always to a given point, under given barometrical pressure; and the mean pressure of 30 inches of mercury is generally understood to be that to which our thermometers are graduated. Sir I. NEWTON employed the freezing and boiling of water as fixed points, but he used linseed oil to fill his tubes, a liquid inconvenient from its viscosity, and irregularity of expansion. Alcohol was first used by the Florentine Academicians, because it is very sensible to changes of temperature, and remains clear in the tube; but, since its boiling-point is much below that of water, it is useless for the measurement of high temperatures, though, from not freezing, well suited to indicate extreme cold. For general convenience and equability of expansion, mercury, first used, I believe, by Dr. HALLEY, takes precedence of all other liquids. It bears nearly a red heat before it boils, and sustains the cold of these latitudes without freezing; hence it is the liquid generally used for accurate and delicate thermometers.

The principal thermometric scales in use in Europe are, FAHRENHEIT'S, which commences at the temperature produced by mixing snow and salt, and which is 32° below the freezing of water; so that the latter point is marked 32° , and the boiling-point 212° , the intermediate space being divided into 180° : REAUMUR'S, in which the zero is the freezing-point, and 80° the boiling-point: and the *Centigrade*, in which the space between the freezing and boiling of water is divided into 100° , the freezing-point being 0° and the boiling-point of water 100° .

In this country, FAHRENHEIT'S scale is in general use; over the greater part of Germany, REAUMUR'S scale is employed; and in France, the *Centi-*

* *Essays, Medical and Philosophical.*
By G. MARTINE, M.D. London, 1740.

† *Phil. Trans., Abr., ii. p. 36.*

grade: it is much to be desired that the subject of a thermometric scale should, in the present advanced state of science as regards the doctrine of heat, be taken into consideration, and that either the *Centigrade* (which is certainly the least objectionable of those hitherto used) or some analogous scale, should be universally employed.

There are other circumstances connected with the construction and indications of the thermometer, which I reserve for notice till we consider the more refined investigations relating to the subject of heat, undertaken at a subsequent period: in the meantime we may advert to the discovery of a singular property possessed by *water*, which, as far as concerns the influence of heat upon it, distinguishes it from other liquids. This anomaly was first observed by the Florentine Academicians: "We know," they say, "that water, in passing into the state of ice, suffers great expansion, a fact sufficiently evident from the violence with which various vessels are broken and rent asunder during the freezing of water in them; but it was not known to us at what particular period of refrigeration this expansion occurs; nor could we learn it from our former experiments, which were made in vessels of silver, gold, brass, and other strong, but opaque materials. We, therefore, now employed glass flasks, and observed, that the moment they were immersed in ice, the water in the neck of the flask was suddenly elevated, that it then began gradually to fall, and at length remained for a few moments quite stationary; then it began again to rise with a slow, but apparently equable progress at first, but afterwards sprung up so suddenly, that the eye could scarcely follow it*."

In BIRCH's *History of the Royal Society*, under the date of the 6th of February, 1683, we find some experiments on the freezing of water made

* The following unaffected narrative of this celebrated experiment is very different from the usual verbose and pompous style of the philosophers of the period.

"Già sapevamo per innanzi (e lo sa ognuno) che il freddo, da principio, opera in tutti i liquori ristignimento, e diminuzione di mole, e di ciò non solamente n'avevamo la riprova ordinaria dell'aquazente de' Termometri, ma n'avevamo fatta esperienza nell'acqua, nell'olio, nell'argentovivo, ed in molt'altri fluidi. Dall'altro canto sapevamo ancora, che nel passaggio, che fa l'acqua dall'esser semplicemente fredda, al rimoversi dalla sua fluidità, e ricever consistenza e durezza coll'agghiacciamento, non solo ritorna alla mole, ch'ell'aveva prima di raffreddarsi, ma trapassa ad una maggiore, mentre se le veggon rompere vasi di vetro e di metallo con tanta forza. Ma qual poi si fosse il periodo di queste varie alterazioni, che in essa opera il freddo, questo non sapevamo ancora, ne era possibile d'arrivarvi con agghiacciarla dentro a' vasi opachi, come quei d'ar-

gento, d'ottone, e d'oro, ne' quali s'era fin' allora agghiacciata: Onde per non mancare di quella notizia, che pareva esser l'anima di tutte quest'esperienze, ricorremmo al cristallo, ed al vetro, sperando per la trasparenza della materia d'aver presto add'assicurarci come la cosa andasse, mentre si poteva a ciascun movimento, che fosse apparso nell'acqua del collo, cavar subito la palla dal ghiaccio, e riconoscer in essa quali alterationi gli corrispondessero. Ma la verità si è, che noi stentammo assai più che non ci saremmo mai dati ad intendere, prima di poter rinvenire alcuna cosa di certo intorno a' periodi di questi accidenti. E per dirne più distintamente, il successo è da sapere, che nella prima immersione, che facevamo della palla, subito, ch'ella toccava l'acqua del ghiaccio, s'osservava nell'acqua del collo un piccolo sollevamento, ma assai veloce, dopo il quale con moto assai ordinato, e di mezzana velocità, s'andava ritirando verso la palla, finchè arrivata a un certo grado, non proseguiva più oltre a discendere, ma si fermava quivi per qualche tempo, a

before that body, in consequence of a letter received from Mr. MUSGRAVE, of Oxford. “Dr. CROUNE said, he had observed water put into a bolt-head rise higher before freezing. Mr. HOOKE attributed this to the shrinking of the glass. Dr. C. said, the glass had been long in the cold before, and the water rose immediately. Dr. WALLIS proposed that an empty glass might be well cooled in a freezing liquor, in order that it might have its contraction before the water be put into it. This was done immediately by Mr. HUNT, and the water being put into a small bolt-head rose in the neck.” Numerous and correct experiments have completely established this peculiarity in the freezing of water; other fluids have their maximum of density just before the freezing-point; water expands before it freezes, and consequently water at 36° is lighter than water at 40° , and floats upon its surface; hence it is, that large masses of water, being cooled by the atmosphere upon their surface, only freeze there, and the water beneath retains the more congenial temperature of 40° .

Among the experiments made by the *Accademia del Cimento*, we find many details independent of those already adverted to, which are at once accurate and curious, and especially in that section of their *Transactions*, entitled *Experiments relating to Ice*. In the sixth experiment of this section, they notice the effect of various metallic vessels upon the thawing of ice: they found it was longer preserved in lead and tin, than in similar vessels of brass and of iron; and that it soon thawed in gold, and sooner in silver. This enumeration of the metals is in the order of their conducting power, as ascertained more than a century afterwards by Dr. INGENHOUSZ.

The radiation, reflection, and refraction of heat, are subjects of inquiry which also probably engaged much of the attention of the Florentine experimentalists, but their published essays contain scarcely any details relating to them. In the ninth experiment, however, of the above quoted section, they have given an account of a discovery that afterwards excited much discussion, relating to the reflection and radiation of cold. “We were anxious to try if a concave mirror, placed before a mass of ice, weighing five hundred pounds, caused any reflection of cold upon a very delicate thermometer placed in its focus; and truly it began immediately to fall; but in consequence of the vicinity of the ice, it was doubtful whether the effect resulted from the direct, or from the reflected rays; we, therefore, covered the mirror, and whatever was the cause, certain it is that the spirit began immediately to rise again. With all this, we do not mean positively to affirm that no other cause could have produced such an effect, than the absence of the rays reflected from the mirror, for we were not careful in adopting all the precautions requisite in such an experiment*.”

giudizio dezli occhi, affatto priva di movimento. Poi a poco a poco si vedea ricominciare a salire, ma con un moto tardissimo, e apparentemente equabile, dal quale senz' alcun proporzionale acceleramento spiccava in un subito un furiosissimo salto, nel qual tempo era impossibile tenerle dietro coll' occhio, scorrendo con quell' impeto, per così dire,

in instanti le decine e le decine de' gradi.” *Esperienze intorno al progresso degli artificiali agghiacciamenti, e de' loro mirabili accidenti*. Saggi di naturali esperienze fatte nell' accademia Del Cimento. Firenze, 1691.

* *Saggi*, above quoted. See also Waller's Translation of the *Essays of the Academicians del Cimento*. 1684.

MUSCHENBROEK, DE MAIRAN, and others, concluded from these and similar experiments, that cold is not the mere absence of heat, but a distinct form of matter possessed of specific properties. Sometimes it has been spoken of as a substance of a saline nature, floating in minute particles in the air, and occasioning the congelation of water by intruding themselves among its particles. Now, although such a conclusion is not called for by the phenomena, it has been plausibly conjectured that ice and other cold bodies do radiate matter, which is capable of exciting the sensation of cold in circumjacent bodies.

To get rid, however, of such an hypothesis, it has been suggested that the effect of the ice is to disturb the balance of temperature in the surrounding bodies, and consequently to cause a chasm, as it were, into which they tend to pour their excess of heat; among these is the thermometer, which consequently indicates cold: but although such an explanation might suffice in respect to the mere approximation of the ice to the thermometer, it is scarcely applicable to the case of radiation.

Sir H. DAVY says, "The apparent radiation of cold is in harmony with the phenomena of the reflection of the solar beams; for if it be supposed that rays capable of producing heat emanate from all terrestrial bodies, but in quantities greater in some increasing proportion as their temperatures are higher, then the introduction of a cold body into the focus of one mirror ought to diminish the temperature of a thermometer in the focus of the other, in the same manner as a black body placed in one focus would diminish the quantity of light in the other focus; and the eye is to the rays producing light, a measure similar to that which the thermometer is to rays producing heat*."

LESLIE admits that the temperature excited by radiant matter varies with its source, and that all substances may be considered as producing these emanations. If we approach a heated surface, we feel the radiant heat; if the surface be of the same temperature as ordinary circumjacent bodies, or of a temperature between 40° and 80° , we feel, perhaps, nothing remarkable; yet such a surface does actually radiate matter of its own temperature, as shown by approaching it with a cooler thermometer: if the surface be of ice or colder materials, we feel upon approaching it the sensation of cold, depending upon the emanation of cold radiant matter, since it is susceptible of reflection by the mirrors. We are further to consider, that the terms *heat* and *cold* are merely relative. We may suppose that in an atmosphere heated to 400° , boiling water would radiate (comparatively speaking) cold; and in the same way ice at 32° would radiate heat in an atmosphere very much below the freezing-point. To LESLIE we are indebted for an admirable series of researches on the philosophy of radiant matter, partly contained in his *Treatise on Heat*, and partly in other essays. (*Suppl. to Encyclop. Brit.*) He supports the theory of the radiation of cold by some striking illustrations.

§ VIII.

FROM the preceding details, some idea may be formed of the state of Chemistry at the close of the seventeenth century. As an art, we have

* *Elements of Chemical Philosophy*, p. 206.

seen with what success and diligence it was cultivated by BASIL VALENTINE and GLAUBER; and how ably it was pursued as a science by MAYOW and HOOKE. To these philosophers, and to a few of their companions, we not only owe the materials which were arranged and embodied by their earliest successors in the eighteenth century, but we are to ascribe also to them the merit of founding scientific chemistry; of laying the basis upon which the superstructure of modern chemical science has been raised. The importance of multiplied observations and experiments, the application of chemical principles to agriculture, and the aid to be derived from them in several arts and manufactures, as well as in many departments of domestic economy, are to be learned in the writings of GLAUBER; while BASIL VALENTINE and VAN HELMONT have shown the necessity of studying pharmacy on chemical principles, and have applied, with much success, the doctrines learnt in the laboratory, to the preparation of many invaluable medicines, which have facilitated the treatment and cure of disease; nor were the quackery and eccentricities of PARACELSUS unemployed in this reformation. In that age, example was more efficacious than precept; and those who witnessed the cures which he performed, enlisted under his banner, and were equally vehement with their leader in combating the doctrines of the Galenical school of physic, and substituting those of the chemical sect.

If we look at the scientific generalizations of modern chemistry, and more especially at the theories of combustion and acidification, promulgated by the French school about the middle of the last century, we find them not anticipated merely, but even minutely explained, by BOYLE, HOOKE, and MAYOW, who flourished about one hundred years before LAVOISIER; and MAYOW, in his researches into the laws and phenomena of chemical affinity, seems to have trodden upon ground which even NEWTON explored as his own. In the history of chemistry, we perceive, perhaps, more than in any other branch of science, the different roads by which the human mind arrives at the same conclusions; but we are not therefore to consider those conclusions as unavailing, because anticipated; the very circumstance of attaining them by different means, justifies the search; and he whose investigations disclose new views, and unfold new truths, may rest satisfied that he has not laboured in vain, because he ultimately arrives where others have been before him. In estimating, however, the true merits of chemical discoveries and inventions, and more especially in determining the excellence and originality of theories, it is requisite to look to their sources, and to examine the steps which led to them, and upon that examination to found our opinion.

The leading feature and important novelty of the science, as influencing its progress in the last century, was certainly the discovery of gaseous bodies, and the perfection of pneumatic chemistry; without which analysis could have made little progress, and, independent of which, all improvement in theory would have been but slow and ineffectual; it was also materially, though less directly assisted by those investigations respecting the agency of heat, in which Dr. BLACK made himself so eminent.

Though something is due to MAYOW, we must in justice confer the merit of founding *pneumatic chemistry* upon Dr. STEPHEN HALES*, whose

* Born in Kent, 1677; died at Teddington, 1761.

researches came before the public very early in the last century. "He refused a canonry of Windsor, that he might continue to devote himself to his parochial duties, and favorite scientific pursuits; and, as piety, truth, and virtue, were the principles of his character, he lived in universal esteem, to the age of eighty-four, dying at Teddington, on the 4th of January, 1761, where he was buried, under the church-tower, which he had rebuilt at his own expense."

Dr. HALES commenced the communication of his researches to the Royal Society about the year 1717, and in 1727 he published his *Statical Essays, containing an Essay towards a Natural History of Vegetation, of use to those who are curious in the Culture and Improvement of Gardening: also a Specimen of an Attempt to analyse the Air, by a great variety of Chemico-Statical Experiments, which were read at several Meetings before the Royal Society*. In 1733, a second volume of these Essays was published, containing *Hæmastatics, and Experiments on the Stone of the Kidney and Bladder*. Of these Essays, it will be first necessary to advert to the contents of those relating to the *analysis* of the air, a term, by the way, which by no means well applies to the researches they contain.

Dr. HALES employed several methods of collecting and examining the gaseous products of a variety of bodies, many of which approach those at present in use. Sometimes he placed substances upon a stand, under a bell-glass inverted over water; or he employed a flask to contain the materials producing aëriform matter, over which was placed a bell-glass, the whole being confined over water as before. Or where a high temperature was required for the production of the gaseous bodies, he used an iron retort formed of a bent gun-barrel, and received the air into a vessel inverted in a tub of water. In the modification and management of these forms of apparatus, he displayed some ingenuity; but it should be remembered that he was anticipated in the greater number of his contrivances by MAYOW, as we have already had occasion to remark.

In prosecuting his inquiries by these means, Dr. HALES stumbled upon a variety of curious facts and observations; but having unluckily predetermined that the various products formed were mere modifications and contaminations of common air, he let slip a numerous series of discoveries once fairly within his grasp, and which were afterwards eagerly amassed and successfully reasoned upon by PRIESTLEY and his contemporaries. Thus, Dr. HALES observed that phosphorus, when burned, absorbed air, and produced white fumes; but he neglected any examination of the product and of the residue. He distilled air from wood, and found it fatal to animals; from Newcastle coal he obtained one-third its weight of gas; from nitre, one hundred and eighty times its bulk; and from salt of tartar urged by an intense heat, he also procured aëriform matter; but in no one instance did he examine these gaseous products with the attention that might have been expected from an experimentalist so diligent and original. He found that iron filings and oil of vitriol produced scarcely any air; but that, upon the addition of water, gas was abundantly evolved from such a mixture. Here he obtained *hydrogen*, but instead of stopping to examine its properties, he hastens on to irrelevant observations, and seems always eager rather to multiply experiments

than to examine their results. Upon the same principle, he accurately details the quantity of air generated by distilling hog's blood, tallow, sal ammoniac, oyster-shells, Indian wheat, pease, mustard-seed, amber, tobacco, sugar, bees' wax, and gall-stones; and yet, from such numerous experiments, he scarcely draws a single inference that deserves to be recorded.

In his experiments on respiration, Dr. HALES obtained results of such interest, that one is surprised at the coldness with which he pursued them, and the carelessness with which he drops the inquiry. Finding that a given portion of air could only be respired for a given time, and that it soon produced oppression and difficulty of breathing, in consequence, as he says, "of the gross and sulphureous vapours with which it becomes loaded," he endeavoured to discover some substance which, by absorbing those vapours, might render respired air more fit for breathing, and consequently contribute to its purification in small and crowded rooms, and other similar situations. The apparatus which he used in these researches was sufficiently ingenious; it consisted of a bag made of bladder, with a mouth-piece so supplied with valves as to oblige the air breathed into it to traverse its whole length, before it could return to the lungs. He found that he could breathe the air contained in this apparatus to and fro, for a minute and a half; he then wetted certain diaphragms or partitions of flannel in the bag, with different liquids, and found that he was thus enabled to respire the confined air for rather a longer time; but having dipped them in a solution of highly calcined tartar, he found he could, without much inconvenience, continue the breathing for eight minutes and a half.

It is probable that the air was purified in this instance by the absorption of the carbonic acid; or to use Dr. HALES' language, "of the sulphureous gross vapors;" but, unwilling as he always appears to follow up and investigate the new facts, he says, that the effect was perhaps owing to the bladder and syphon being entirely dry, or to some unheeded passage for the air through the ligatures; "neither did I care to ascertain the matter by repeated experiments, fearing I might thereby some way injure my lungs." He however weighed the diaphragms, and found that they had increased in weight about thirty grains in five minutes, making the quantity of matter absorbed by them from the expired air, amount to nineteen ounces in twenty-four hours. In other experiments, the author notices the purification of air spoiled by the burning of candles and of brimstone, by the action of calcined tartar; but he takes no pains to inquire into the specific action of the salt, and confounds it with that of saline bodies generally.

But Dr. HALES' researches relating to the motion of sap in vegetables, are in a great measure free from the objections which may be made to his other experimental inquiries, and were pursued upon a more regular and digested plan. His first object seems to have been to ascertain the quantities of matter imbibed and perspired by plants and trees; for this purpose he grew a sunflower in soil contained in a tight box, and watering it with given weights of water, he ascertained the quantity that it daily lost by transpiration from the leaves: after stating the extent of surface of the leaves, he informs us, that its minimum of loss by that

channel was sixteen ounces, and its maximum twenty-eight ounces, in a day of twelve hours. To ascertain more particularly the influence of the leaves upon the absorption of water by the root, two branches, one with and one without leaves, were put into separate glasses, containing known quantities of water. The boughs with leaves absorbed on an average from twenty to twenty-five ounces in a day, and were lighter at night than in the morning; those without leaves imbibed but one ounce, and were heavier in the evening than in the morning. This experiment led to the inference, that the ascent of the sap, and the quantity of matter absorbed from the soil, are much influenced by the leaves; "and accordingly I observe," he says, "that the leaves next adjoining to blossoms are in the Spring very much expanded, when the other leaves on barren shoots are but beginning to shoot; and that all peach-leaves are pretty large before the blossom goes off: and that in apples or pears, the leaves are one-third or half-grown before the blossom blows: so provident is Nature in making timely provision for the nourishing of the yet embryo fruit." A certain degree of dryness of air is requisite to promote the due transpiration by the leaves, for when too much moisture hovers about the plant, it hinders the kindly action of the leaves, "whereby," says Dr. HALES, "the stagnating sap corrupts and breeds mouldy fen, which often spoils vast quantities of flourishing hop-grounds. This was the case in the year 1723, when ten of fourteen days, almost continual rain fell, about the latter half of July, after four months' dry weather; upon which the most flourishing and promising hops were all infected with mould or fen in their leaves and fruit, while the then poor and unpromising hops escaped and produced plenty, because they being small did not perspire so great a quantity as the others." "This rain on the then warm earth made the grass shoot out as fast as if it were in a hot-bed, and the apples grew so precipitately that they were of a very flashy constitution, so as to rot more remarkably than has ever been remembered."

In the course of his experiments upon the transpiration of plants, and their absorbing powers, Dr. HALES endeavoured, but always without success, to alter the flavor of their fruit by causing them to imbibe various perfumes. He placed a vessel upon a divided branch of a tree, so that it might absorb any fluid contained in it. Upon filling it with camphorated spirit of wine, the whole branch of an apple tree was killed; but though the apples hung several weeks afterwards, no alteration of taste was perceived in them, though the smell of camphor was strong in the leaf stalks, and all other parts of the dead branch. Different perfumed waters were absorbed by fruit trees without injuring them, but they failed to confer any peculiar flavor on the fruit.

If, as Dr. HALES' experiments seemed to show, the transpiration of plants, and the motion of the sap, as well as the absorption from the soil, depend upon the leaves, it became an interesting question to examine these points in evergreens; and he found that they absorbed less and transpired considerably less than other trees: hence, "the cedar of Libanus, and the ilex or evergreen oak, grafted on an English oak, and on a larch, were verdant all the Winter, though the leaves of the oak and larch decayed, and fell off as usual; the fact being, that evergreens live and thrive with very little nourishment."

Having proved that trees transpire large quantities of matter, our author next endeavoured to collect and examine it: he caused the branches and leaves to be enclosed in flasks and retorts; he placed a large sun-flower under the head of an alembic, and thus procured "what appeared to be pure water, very slightly tainted by vegetable matter; it seemed not to differ, though obtained from different plants." After some observations respecting the moisture and temperature of the earth, Dr. HALES proceeds with experiments to determine the force with which trees imbibe moisture, and here he obtained some striking results. He exposed the roots of a pear-tree, and cut off the end of one, half an inch diameter; the stump was cemented into the upper end of a tube twenty-six inches long, filled with water, and dipping at its lowest extremity into mercury. The root imbibed the water so vigorously, that in six minutes' time the mercury rose eight inches in the tube. This experiment was made in August. Another experiment, similarly contrived, in which a large branch of the root of an apple-tree was used, the diameter of its transverse section being three-fourths of an inch, caused the mercury to ascend five inches in half an hour. The oozing of air-bubbles from the cut surface interfered with the rise of the fluid in these tubes, but it was observed that the mercury rose highest when the sun was clear and warm; towards evening it subsided three or four inches, and rose again the next day. It also subsided during rain. This experiment was made in May. When we consider, says Dr. HALES, that the power thus required to raise mercury twelve inches, would raise water thirteen feet eight inches, we may form some idea of the power exerted by the growing vegetable.

Dr. HALES was one of the first who noticed the influence of cutting a ring of bark off the branch of a tree, (or *ringing*, as it is now technically called,) upon the growth of its fruit and leaves; but instead of attributing its effect to an accumulation of sap, the juice being prevented flowing downwards in the vessels of the bark, he refers it to a less quantity of sap arising, "whence it is better digested and prepared for the nourishment of the fruit;" he combats the notion of the sap *circulating* in trees, and imagines that it is often progressive at one time, and retrograde in another, in the same vessels.

Dr. HALES concludes his Vegetable Statics, with an account of some experiments to prove that a considerable quantity of air is inspired by plants, and with some observations on the growth of seeds and vegetables generally. By cementing a branch with its leaves, into a glass tube dipped into water, he observed the liquid rise in the tube, in consequence of the absorption of the confined air; and on putting a piece of the stem of a birch-tree under the receiver of an air-pump, he extracted abundance of air-bubbles from it during the exhaustion. He refers the first growth of a seed to the absorption of moisture, which swells it, and, as he thinks, protrudes nourishment into the radicle, which soon becomes capable of absorbing moisture from the soil; the root, he says, by expanding, carries the seed-lobes upwards with the plume, where they expand into leaves, which are of such importance to the tender plume, that it perishes on their removal; which renders it probable that they do the same office to the plume, that the leaves adjoining to apples, quinces, and other fruits do to them, namely, draw the sap within reach of their attraction. As

the tree advances in stature the different lateral branches shoot out, "each lower order being longer than those immediately above them, not only on account of primogeniture, but also because, being inserted in larger parts of the trunk, and nearer the root, they have the advantage of being served with greater plenty of sap; hence arises the beautiful parabolical figure of trees. But when trees stand thick together in woods or groves, this their natural shape is altered, because the lower lateral branches being shaded, they can transpire little, and therefore, drawing little nourishment, they perish; but the top branches being exposed to a free drying air, they transpire plentifully, and thereby drawing the sap to the top, they advance much in height; but if, when such a grove of tall trees is cut down, there be left here and there a single tree, that tree will then shoot out lateral branches; the leaves of which branches now transpiring freely, will attract plenty of sap, on which account the top, being deprived of its nourishment, usually dies."

Such are the leading objects of inquiry which engaged the attention of Dr. HALES; and, if we consider the little progress that had been previously made in pneumatic chemistry, we must allow that he much promoted that department of research: in his inquiries into the functions of vegetables he was at once original and acute, and laid the foundation of a very useful and curious series of investigations, which DUHAMEL, ANDREW KNIGHT, and others, have pursued with so much success. HALES entered into some collateral branches of investigation, the results of which are given in the *Philosophical Transactions*, and are collected in the second volume of his *Essays*; but they are not of such importance as to form any prominent feature in a general history of his discoveries.

When it is recollected that HALES wrote at the commencement of the last century, that there were then very few models of scientific composition extant that were worth copying, and that a pompous and obscure style of writing was prevalent among his experimental contemporaries, we cannot but admire the perspicuous and unadorned manner in which he details his facts and observations: he has all the merit that in this respect belongs to BOYLE, without his diffusiveness; and a pleasing vein of sound and unaffected morality accompanies his argument, and leads him, whilst endeavouring to unveil the mysteries of Nature, to direct our attention, with becoming modesty, to the penury of man's wisdom, when compared with the admirable adjustment of causes and effects discoverable in her lowliest works.

Contemporary with HALES was the celebrated HERMANN BOERHAAVE of Leyden, a man who laid medicine and chemistry under deep obligations; the former, by his successful practice, and happy method of instruction; the latter, by diligently experimenting in some of its most difficult departments. "He prosecuted chemistry," says Dr. JOHNSON, "with all the ardour of a philosopher whose industry was not to be wearied, and whose love of truth was too strong to suffer him to acquiesce in the report of others." BOERHAAVE's original chemical investigations were nearly of the same nature as those of HALES: he experimented upon the gaseous products afforded by a variety of vegetable and animal substances; he attributed the elasticity of air to its union with fire, and considered its ponderable matter as susceptible of chemical combinations. In disclosing

these views, he has certainly sketched an outline of one of the modern theories of combustion; but he went no further, and was not more successful than HALEs, in discriminating between common air, and the various gaseous products that resulted from some of his experiments. His writings are enumerated in chronological order in the masterly sketch of his life, written by Dr. JOHNSON; "they have," says his biographer, "made all encomiums useless and vain, since no man can attentively peruse them, without admiring the abilities, and reverencing the virtues, of the author." His only chemical work, entitled *Elementa Chemiæ*, was first published in 1732. It contains an useful essay on the History of the Science*.

§ IX.

THE names of BLACK and BERGMAN, with a host of others, either forgotten, or eclipsed by those eminent philosophers, occur in the division of our history at which we have now arrived, and which embraces its progress in the interval between the researches of HALEs, and those of PRIESTLEY. Chemistry now assumed a more important and interesting aspect: the facts already collected began to be digested and arranged, and active measures were taken to embody the scattered materials that presented themselves; to ascertain their relative value; to reject those which were unimportant or useless; and to select such as deserved to be dignified with the title of standard authorities. Dr. BLACK's researches possess a two-fold interest, for he not merely made important contributions to the facts of the science, but also established a new theory, connected with one of the most intricate of its subjects, heat.

Dr. JOSEPH BLACK was sprung from a Scottish family, transplanted first to Ireland, and then to France, where he was born in 1728, on the banks of the Garonne. When twelve years of age, he was sent for

* Boerhaave was born in December, 1668, at a village near Leyden. He died in September, 1738. He was an eminent ornament of medicine, as well as of chemical science. His oration upon resigning the office of Governor of the University of Leyden has been justly eulogized by Johnson. (*Life of Boerhaave*.) "He here declares in the strongest terms (says his eloquent biographer) in favour of experimental knowledge, and reflects with just severity upon those arrogant philosophers, who are too easily disgusted with the slow methods of obtaining true notions by frequent experiments, and who, possessed with too high an opinion of their own abilities, rather choose to consult their own imaginations than inquire into nature, and are better pleased with the charming amusement of forming hypotheses than the toilsome drudgery of making observations.

"The emptiness and uncertainty of all those systems, whether venerable for

their antiquity, or agreeable for their novelty, he has evidently shown; and not only declared, but proved, that we are entirely ignorant of the principles of things, and that all the knowledge we have is of such qualities alone as are discoverable by experience, or such as may be deduced from them by mathematical demonstration."

Boerhaave's contributions to physic were large and valuable. His *Elementa Chemiæ*, of which a good translation, with notes, was edited in 1753 by Dr. Shaw, he dedicated to his brother, who was intended for the medical profession, but went into the church; while Boerhaave, who originally studied divinity, relinquished it for physic and chemistry. Alluding to this circumstance, "Providence," says he, "has changed our views, and consigned you to religious duties, while I, whose talents were unequal to higher objects, am humbly content with the profession of physic."

education, to Belfast, and afterwards to the University of Glasgow, where he entered upon the study of Physic, under the guidance of that bright ornament of medical science, Dr. WILLIAM CULLEN. In 1750, he removed to Edinburgh; four years afterwards, he took the degree of Doctor of Physic; and, in 1756, published his Experiments on Magnesia, Quicklime, and some other alkaline substances, in the *Physical and Literary Essays*. In the same year, CULLEN having removed to Edinburgh, BLACK returned to Glasgow, to fill the medical and chemical chair of that University, where he was received with open arms both by the classes and professors. In 1764, he brought his ideas respecting the combinations of heat with ponderable matter, to maturity. Speculations upon this subject had occupied his mind during a considerable period, but the difficulties of the inquiry, and the time necessarily consumed in other professional avocations, had considerably interfered with the pursuit. In 1766, he was appointed to the chemical chair of Edinburgh, an office which he filled with such talent, industry, and perseverance, as not only drew an immense concourse of hearers to his class, but tended to confer upon chemistry a degree of popularity and importance, which has been greatly conducive to its promotion and extension. "His discourse," says his biographer, Professor ROBISON, "was so plain and perspicuous, his illustrations by experiment so apposite, that his sentiments on any subject never could be mistaken; and his instructions were so clear of all hypothesis or conjecture, that the hearer rested on his conclusions with a confidence scarcely exceeded in matters of his own experience*." In short, Dr. BLACK, in his professorial capacity, was entitled to every praise, and he contributed most essentially to the foundation and increase of the reputation which the University of Edinburgh has acquired and maintained. Nor was his private character at variance with his public excellence; he was mild, amiable, and fond of conversation, whether serious or sportive; and united, to the highest philosophical attainments, most of the elegant accomplishments of life. In his advanced age he often expressed a hope that he might not linger in protracted sickness, on account of the distress which, in such cases, is suffered by attending friends; and

* Dr. Black's character as a lecturer is given by his friend Professor Robison in the following terms:—"He endeavoured every year to render his courses more plain and familiar, and to illustrate them by a greater variety of examples in the way of experiments. No man could perform these more neatly and successfully. They were always ingeniously and judiciously contrived, clearly establishing the point in view, and never more than sufficed for this purpose. While he scorned the quackery of a showman, the simplicity, neatness, and elegance with which they were performed, were truly admirable. Indeed, the *simplex munditiis* stamped everything that he did. I think it was the unperceived operation of this impression

that made Dr. Black's lectures such a treat to all his scholars. They were not only instructed, but (they knew not how) delighted; and without any effort to please, but solely by the natural emanation of a gentle and elegant mind, co-operating indeed with a most perspicuous exhibition of his sentiments, Dr. Black became a favourite lecturer; and many were induced, by the report of his students, to attend his courses, without having any particular relish for chemical knowledge, but merely in order to be pleased. This, however, contributed greatly to the extending the knowledge of Chemistry, and it became a fashionable part of the accomplishments of a gentleman."—*Preface*, p. li.

his death, which happened in his seventy-first year, in November, 1799, is on this account the more remarkable. He was taking some milk and water, and having the cup in his hand, when the last stroke of his pulse was to be given, had set it upon his knee, and in this attitude expired without the smallest agitation.

The writings of BLACK, though few, are masterpieces of scientific composition. Newton was his model, and he was the first who transferred into chemistry the severe system of inductive logic, which marks the productions of that great master. "In no scientific inquiries, since the date of the *Principia* and *Optics*, do we find so great a proportion of pure ratiocination, founded upon the description of common facts, but leading to the most unexpected and important results, as in the two grand systems of BLACK." Averse to all hypothesis, and aware of the multitudinous facts upon which a theory, that is to stand firm, must be founded, Dr. BLACK was unwarrantably slow in the formal public disclosure of his researches. His tenets were fully and freely delivered to his pupils; but he rarely intruded upon the public as an author; and his achievements in the philosophy of heat are chiefly developed in his posthumous works. This silence, arising out of an overcautious modesty which marked all his proceedings, was not favorable to the reputation of Dr. BLACK. Faulty and incomplete copies of his lectures were circulated among his friends and admirers, which afterwards reached the hands of those who deserved another name, and by whom they were not very honorably employed.

When BLACK first entered the precincts of chemistry, there was a busy and acute controversy respecting the cause of causticity in earths and alkalis; it was supposed by STAHL that the conversion of limestone into quicklime depended upon its absorbing certain igneous particles; by MACQUER*, MEYER†, and others, the change was referred to an acrid

* Macquer was born at Paris in 1718, and died in 1784. He ranks among the most eminent scientific chemists of the early part of the eighteenth century; and though involved in the errors of the Phlogistic school, he has written with much good sense and perspicuity on a variety of chemical subjects. His most celebrated works are, the *Elemens de Chimie Théorique*, Paris, 1749; and *Elemens de Chimie Pratique*, Paris, 1751. He also published a Chemical Dictionary. The following is all his information respecting the property possessed by quicklime of rendering the alkalis caustic. After describing the process, he observes, "Le but de cette opération, est de réunir avec le sel alcali fixé ce que la chaux a de salin et d'âcre."—"On le combine avec la partie la plus âcre, la plus subtile, et la plus saline de la chaux."—"Nous n'entreprendrons point ici d'expliquer pourquoi le sel alcali, que l'on combine avec la chaux, acquiert une si grande causticité. Cette question nous paroît une des plus délicates et des plus difficiles à résoudre que nous

offre la Chimie. Elle tient à celle des propriétés alcalines de la chaux, et on ne peut guères espérer de la résoudre, que quand on aura acquis sur la nature de cette substance, beaucoup plus de lumières que nous n'en avons à présent."—*Elemens de Chimie Pratique*, pp. 179, 180.

† J. F. MEYER'S *Chemische versuche zur nähern erkenntniss des ungelöschten kalks; der elastischen und electrischen Materie, des allerreinsten feuerwesens, und der ursprünglichen allgemeinen saure*. Hanover, 1764. In this dissertation, though published subsequently to Black's essay, the causticity of the alkalis and lime is referred to the absorption of a principle which the author calls *Cauticum*, or *Acidum pingue*. Between the years 1760 and 1772, a great variety of dissertations were published in Germany upon this question, some in support of Black's doctrines, others in favor of Meyer's hypothetical absurdities. See GREN'S *Systematisches Handbuch der Gesammten Chemie*. Halle, 1794. § 437. —*Observ. Phys. Chem.*, 1722.

acid, contracted in the fire; by others, to nondescript saline particles. Dr. BLACK's notice appears to have been drawn to this inquiry, by the researches of HOFFMAN* concerning the nature of magnesia: he found that when that earth was obtained by adding a mild alkali to solution of Epsom salt, it effervesced upon the addition of an acid; but that if heated red-hot, it no longer effervesced, and moreover lost considerably in weight. The same fact applied equally to lime, and led him to believe, that that substance, instead of acquiring its acrimony by the absorption of something from the fire, became caustic by the loss or expulsion of one of its elements, in consequence of being heated. He then distilled some magnesia in a retort; but finding that, though it diminished considerably in weight, the only visible loss it sustained was a minute portion of water, he conceived the possibility of the escape of some gaseous matter; and, on mixing common magnesia and an acid in a proper phial, he collected a considerable quantity of a permanently elastic gaseous body: from chalk or limestone, and from the mild alkalis, he procured a similar gas, and he termed it *fixed air*.

In 1764, Dr. MACBRIDE, of Dublin, verified and extended these researches; he found that quicklime, after having been exposed to air, acquired the property of effervescing, and, consequently, fixed air must exist in the atmosphere†. He also explained the agency of lime as a manure, and introduced some important improvements into the art of tanning.

In 1765, Dr. BROWNRIGG threw out some curious hints upon the same subject: in a communication to the Royal Society, printed in the *Transactions* for that year, he remarks, "that a more intimate acquaintance with those noxious airs in mines, called *damps*, might lead to a discovery of that subtle principle of mineral waters, known by the name of their *spirit*; that the mephitic exhalations, termed *choak-damp*, he had found to be a fluid permanently elastic; and that, from various experiments, he had reason to conclude that it entered the waters of Pyrmont, Spa, and others, imparting to them that pungent taste, whence they are called *acidulæ*, and likewise that volatile principle on which their virtues chiefly depend;" and in 1760, Mr. LANE remarked the solubility of iron in water impregnated with fixed air.

I shall again have occasion to revert to the nature and properties of *fixed air*, which engaged much of the attention of PRIESTLEY, LAVOISIER, and other celebrated men, whose labors are yet to be noticed, consequently we may proceed to BLACK's researches on the subject of heat, researches which are more exclusively his own, and in which he has dis-

* Hoffman was the most celebrated Chemical Physician of the age. He was born at Halle in Saxony, in 1660, and died in 1742. His writings, which are voluminous, are also valuable. In 1749, they were eked out by the Genevese booksellers, into nine folio volumes. The following are his leading Essays in Chemistry: *Dissertationes de Generatione Salium; De Natura Nitri; De Cinabare Antimonii; De mirabili Sulphuris*

Antimonii fixati efficacia; De Mercurio et Medicamentis Mercurialibus. Observationum, Physico-Chemicarum Collectio.

† MACBRIDE'S *Experimental Essays*, 1764. The merit of this performance induced the University of Glasgow to bestow the degree of Doctor of Physic on the author. He was born in the county of Antrim in 1726, and died in 1778.

played that acuteness and originality which have given his name so high a rank in the annals of chemical science.

In speaking of the experiments of BOYLE, and of the investigations of the Florentine Academicians, two curious circumstances respecting the temperature of thawing ice and boiling water were noticed. It was stated that ice, during its liquifaction, retained an uniform temperature of 32° ; and that water, during its ordinary ebullition, never became hotter than 212° ; hence the use of those fixed points in the graduation of thermometers. We have now to examine the views which these phenomena suggested to Dr. BLACK, and the results that followed his inquiries into their causes and effects.

If a vessel of ice, of any very low temperature, be brought into a warm room, or placed near the fire, or over a small steadily burning lamp, a thermometer placed in it will gradually rise to 32° in the contact of the ice, and not higher, until the whole is melted. Then the temperature of the ice-cold water will begin to rise, and if the lamp be continued under the vessel, it will go on rising till it attains the temperature of 212° , when it again becomes stationary, and remains so during the whole evaporation. It follows, therefore, that heat is concerned in producing two series of changes: That its first effect is to thaw the ice without elevating the temperature; and that it then raises the thermometer till ebullition takes place, after which, it converts the water into vapor, without elevating either its temperature, or that of the vapor. Hence the following particular heads of inquiry suggested themselves: 1. As to the *absorption* of heat during the conversion of solids into liquids, and of liquids into vapors. 2. As to the *evolution* of heat during the converse changes; namely, the condensation of vapors, and congelation of liquids. 3. As to the *quantity* of thermometric heat absorbed and evolved in these different cases.

The disappearance of thermometric, or sensible heat, alluded to in thawing ice, takes place in all corresponding cases of liquifaction; consequently, if a cold solid be mixed with a given weight of the same substance hot, and in a liquid state, the resulting temperature will not be the mean, as would have been the case if both portions had been in the liquid state, but will be considerably below it, a portion of the heat of the hotter body having been, as it were, consumed in liquifying the solid, without affecting its temperature. Thus, equal parts of water at 212° and at 32° , give, on mixture, the mean temperature of 122° . But equal parts of water at 212° , and of snow at 32° , give, upon mixture, a temperature of 52° only, the excess of heat in this instance being concerned in *liquifaction*, not in elevation of temperature. Dr. BLACK considered the lost heat as equivalent to about 140° in the case of the liquifaction of ice; and among his experiments illustrative of this subject, the following may be selected as most relevant and simple:—Two similar globular glass vessels were filled with water, which in one, was afterwards frozen; and in the other, cooled as nearly as possible to the same point; they were then carried into a room of a temperature of 47° , there being no other difference between them, than that the one contained ice, and the other water. In half an hour the vessel of water had acquired the temperature of 40° ; but in the other it required ten hours and a half

to melt the ice, and raise the water to 40° . Now, as the access of heat was the same in both cases, and as this was at the rate of 7° in half an hour, it follows that in twenty-one half hours, (the time required to thaw the ice and elevate the temperature of the water to 40° ,) it would have received $7 \times 21 = 147^{\circ}$. The difference, therefore, between the increase of temperature in the ice and water vessels, with equal accessions of heat, is 140° , which will express the quantity of sensible heat rendered latent by the operation of liquifaction.

As heat is thus required to convert solids into liquids, it follows, that in cases of sudden liquifaction cold will ensue; hence its production during the solution of many saline bodies; and hence, too, the explication of the theory of freezing mixtures. And as liquifaction is a cooling process, so congelation is a process in which heat is evolved. The freezing of large masses of water is actually a heating process to the circumjacent air. In the sudden crystallization of some saline solutions heat is evolved; and water, under certain circumstances, cooled to eight or ten degrees below its freezing point, suddenly rises to 32° upon congelation.

Having thus perspicuously disposed of the theory of congelation and liquifaction, Dr. BLACK turned his observation to the phenomena attendant on the formation of vapor, and there he was equally happy in his inquiries*.

When water is made to boil, the steam which rises from it is not hotter than the water itself, although there be a continuous influx of heat, which therefore must become *latent* in the steam; and consequently steam, and other vapors, may be regarded as compounds of liquids and heat.

To ascertain the thermometrical expression of the latent heat of

* "When we heat a large quantity of a fluid in a vessel, in the ordinary manner, by setting it on a fire, we have an opportunity of observing some other phenomena which are very instructive. The fluid is gradually heated, and at last attains that temperature which it cannot pass without putting on the form of vapor. In these circumstances, we always observe that it is thrown into the violent agitation which we call boiling. This agitation continues as long as we throw in more heat, or any of the fluid remains, and its violence is proportional to the celerity with which the heat is supplied. Another peculiarity attends this boiling of fluids, which, when first observed, was thought very surprising. However long and violently we boil a fluid, we cannot make it in the least hotter than when it began to boil. The thermometer always points at the same degree, namely, the vaporific point of that fluid. Hence the vaporific point of fluids is often called their boiling point. When these facts and appearances were first observed, they seemed surprising,

and different opinions were formed with respect to the causes upon which they depend. Some thought that this agitation was occasioned by that part of the heat, which was more than the water was capable of receiving, and which forced its way through, so as to occasion the agitation of boiling; others, again, imagined that the agitation proceeded from air, which water is known to contain, and which is now expelled by the heat. Neither of these accounts, however, is just or satisfactory; the first is repugnant to all our experience in regard to heat: we have never observed it in the form of an expansive fluid like air; it pervades all bodies, and cannot be confined by any vessel, or any sort of matter; whereas, the elastic matter of boiling water, can be confined by external pressure, as is evident in the experiments made with Papin's digester."

This quotation from BLACK'S *Lectures* (vol. i., p. 153) is inserted to show the state of the argument respecting the phenomena of ebullition previous to his researches.

steam, Dr. BLACK proceeded thus: The time required to elevate a quantity of water to its boiling-point was carefully noted; the same heat was then continued till the whole had evaporated, and the time required also noted. Thus, supposing the accession of heat to have gone on above 212° , in the same ratio as below it, the temperature that the water would have acquired was estimated, whence it was inferred that the loss of sensible or thermometric heat amounted to more than 800° .

The vast evolution of heat during the condensation of steam now admitted of an explanation; and, on estimating the latent heat of steam, by condensing a given quantity in a given weight of water, it appeared to amount to between 900° and 1000° .

About the year 1774 it was observed by CULLEN* that a thermometer, moistened with spirit of wine or ether, sinks many degrees during the evaporation of those fluids: with ether, the thermometer may be made to fall from 60° to 0° . The cause of this is sufficiently explained by BLACK's theory; the ether and spirit readily pass into vapor, which requires a certain quantity of heat for its production: this is taken from the bodies it happens to be in contact with, as from the thermometer, or the hand; hence the cold perceived when these fluids are applied to the body, and the advantage which results from their application in cases of burns and inflammations. These circumstances led CULLEN to accelerate the evaporation of these fluids, by exposing them under the receiver of the air-pump: by placing a flask half full of ether in a tumbler of water, it was found that, during the process of exhaustion, the evaporation was so rapid from the ether in the flask, as to convert part of the surrounding water into ice†.

* "The chemistry of Stahl, as it was cultivated in Germany and France, and other countries of Europe, scarcely aspired beyond the bounds within which it had been circumscribed by its original founder. A few important facts, indeed, were added, but they were either connected with medical preparations, or attracted attention solely as objects of curiosity. The great and tempting field of Philosophical Chemistry lay unexplored, when it was entered upon with ardor by Dr. Cullen, who first perceived its value, and whose genius and industry, had they not been turned into another channel, would, in all probability, have been crowned with the richest discoveries. But, though Dr. Cullen soon abandoned his chemical pursuits, for those of medicine, he was fortunate enough to have initiated into the science a man whose discoveries formed an era in chemistry, and who first struck out a new and brilliant path, which was afterwards fully laid open, and traversed with so much eclat by the British philosophers who followed his career. This fortunate pupil of Dr. Cullen was Dr.

Joseph Black."—THOMSON, *History of the Royal Society*, p. 468.

Dr. Cullen's fame as a promoter of chemistry has been lost in his greater celebrity as a teacher of medicine. "Chemistry," says his biographer Dr. Anderson, "which was, before his time, a most disgusting pursuit, was, by him, rendered a study so pleasing, so easy, and so attractive, that it is now pursued by numbers as an agreeable recreation, who, but for the lights that were thrown upon it by Cullen and his pupils, would never have thought of engaging in it at all."

Cullen was born in Lanarkshire, in 1712, and died at Edinburgh in 1790.

† Dr. Cullen's paper is published in the *Physical and Literary Essays and Observations*, Edinburgh, 1756, vol. ii. It contains the details of many interesting experiments upon the production of cold, and he considers the power of fluids in this respect, as nearly according to the degree of volatility in each. "If to this," says he, "we join the consideration that the cold is made greater by whatever hastens the evaporation, and

The cause of the cold thus produced by evaporation now therefore became apparent, since no vapor can be in any instance formed without a proportionate absorption, or disappearance, of heat; and the theory of cooling by evaporation from surfaces, as in wine and water coolers composed of porous materials, and of cooling by the affusion of spirit of wine, ether, and other rapidly evaporating substances, became at once evident. LESLIE'S experiment on the production of ice by the evaporation of water *in vacuo*, and WOLLASTON'S *Cryophorus*, beautifully illustrate these views, but it would require much more extensive consideration than we can here afford, to trace all the bearings of the highly important investigations in which the name of BLACK is concerned. There is, however, one subject connected with them, upon which it would be improper not to offer one or two remarks: Dr. BLACK, in his published Letters, has said, "I have the pleasure of thinking, that the knowledge we have acquired concerning the nature of elastic vapor, in consequence of my fortunate observation of what happens in its formation and condensation, has contributed in no inconsiderable degree, to the public good, by *suggesting* to my friend Mr. WATT* of Birmingham, then of Glasgow, his improvements on this engine:" meaning the steam-engine, of which he is then speaking. We are not, however, to conclude from these lines, that Dr. BLACK meant to assume any of the merit which exclusively and justly belongs to Mr. WATT; for in the context he gives him all praise for the originality of his invention; and, in his private correspondence, recommends him particularly to assert, clearly and fully, his sole right to the honor of the improvements of the steam-engine; and, further, in a written testimonial given by Dr. BLACK to Mr. WATT, on the occasion of a trial at law in 1797, connected with a piracy of one of his inventions, after giving a brief account of it, he adds, "Mr. WATT was the sole inventor of the capital improvement and contrivance above-mentioned†."

particularly that the sinking of the thermometer is greater, as the air in which the experiment is made is warmer, if dry at the same time, I think we may now conclude *that the cold produced is the effect of evaporation.*"

* The celebrated James Watt was born at Greenock, on the 19th of January, 1736; and died on the 25th of August, 1819, at Heathfield, near Birmingham, in the 84th year of his age.

† This may be the proper place to show in what way the views of Dr. BLACK'S *Theory of Latent Heat* are connected with the improvements of the steam-engine, a subject upon which I must necessarily be brief, as only in part belonging to the object of this history. The Marquess of Worcester is commonly regarded as the inventor of the steam-engine, but his claims are not well authenticated. It is true, that, among the Utopian schemes to be found in his *Century of Inventions*, there is a dark

description of a method of raising water by steam; but we can scarcely see how this was effected, nor are there any data recorded of the success of the contrivance. Be this as it may, he who barely and obscurely hints the possibility of an undertaking, cannot be regarded as forestalling him who successfully carries it into execution; and the first person who, upon decided evidence, constructed an engine for raising water by the alternate force and condensation of steam, was Captain Savary, who also published an account of his invention, in a small tract called the *Miner's Friend*. To enter into a description of this instrument would be irrelative to my present purpose; I therefore, pass on to that of Newcomen, who, in 1705, obtained a patent for an improved steam-engine. It consisted of a boiler, having a cylinder placed upon it, in which was a solid plunger, connected by its rod with a beam and lifting-pump. The plunger

WATT'S *capital improvement*, above alluded to, consisted chiefly in condensing in a separate vessel, and was adopted before he had any clear notion of Dr. BLACK'S investigations; or at least the main experiments upon which this improvement hinged, were previously undertaken.

was elevated by the elastic force of steam admitted from the boiler. The steam-cock being closed, a small stream of cold water was suffered to run into the cylinder, by which the steam was condensed; the pressure of the atmosphere then acting upon the surface of the plunger, forced it to the bottom of the cylinder, whence it was again raised by the re-admission of steam, and so on. In 1717, Mr. Henry Beighton became an improver of the steam-engine; he was probably the first who caused the steam-cock to be opened and shut by the machinery; for a man was obliged to attend Newcomen's engine for this express purpose. A few other improvements were made by different persons, but they did not affect the general action of the engine; the steam was alternately admitted into, and condensed in the main cylinder; and although defects in its power had been noticed, their cause was unknown until 1765, when happily for the prosperity of the arts and manufactures of this country, the subject engaged the keen ingenuity of Mr. Watt. The model of a Newcomen's engine fell into his hands to be repaired, and in this he presently observed the immense loss of steam occasioned by its admission into the cylinder just cooled for condensation; indeed, he went so far as to ascertain, by experiment, that half the steam of the boiler was thus lost. For, having constructed a boiler which showed the quantity of steam expended at every stroke of the engine, he found that it many times exceeded that which was sufficient to fill the cylinder. But the circumstance that excited his greatest surprise was, that the injection water gained infinitely more heat than if a quantity of boiling water, equal to that required to form the steam, had been added to it. It was probably in this dilemma that he consulted Dr. Black; and the explanation of the difficulty will be obvious from the facts detailed in the text. To avail, himself, therefore, of the whole power of the steam, it became absolutely necessary to keep up the temperature of the cylinder constantly at the boiling-point of water; this he was enabled to attain, by connecting with it

another vessel exhausted of air, and, immersed in cold water, into which, when communicated with the cylinder, the steam, being an elastic fluid, instantly rushes and is condensed; and, on closing its connexion with the cylinder, the steam again admitted there now operates with full force, and suffers no further condensation. To carry off the water from the second vessel, which he calls the *condenser*, and to perpetuate the vacuum, Mr. Watt attached to it a pump, by which both the air and condensed water are removed. The engine thus altered, produced the same power as one of equal dimensions on Newcomen's plan, with rather less than one-third the quantity of steam; hence was a considerable hindrance to the use of the engine materially diminished, namely, the expense of fuel.

But great as was this improvement, it forms a small part of the successful achievements of Mr. Watt in this department of mechanics; he amended the apparatus for boring the cylinders, and improved every part of the working gear of the engine; and he infinitely extended its applications and utility, by applying the power of steam to produce motion round an axis; but their enumeration would lead me out of the bounds of chemistry. I, therefore, hasten to the invention which may be said to have perfected the steam-engine. Steam had hitherto only been used to force the piston down,—it was returned by a weight attached to the other end of the beam. Mr. Watt, in 1782, constructed an engine in which steam was used to elevate, as well as to depress the piston, an alternate vacuum being formed above and below it, by the condenser, as before. An engine, upon this plan, executed at Mr. Watt's manufactory, at Soho, near Birmingham, was first employed at the Albion Mills, near Blackfriar's-bridge, London, in the year 1783.

An excellent sketch of the history of the steam-engine will be found in the *Edinburgh Review*, vol. xiii. p. 311, and some valuable additions to the biography of Watt and the history of his discoveries are contained in the *Eloge* of M. ARAGO.

It must be observed here, that Mr. WATT made a variety of curious investigations upon the subject of steam, and of the capacity of bodies for heat (a subject first inquired into by Dr. BLACK, in 1762), in themselves highly important; but these, and his other mechanical and chemical researches, have been obscured by the magnitude of his inventions and discoveries more immediately connected with the perfection of the steam-engine.

If the suspicion of jealousy, of want of candor, or of any deviation from the strictest veracity, could, by any possibility, attach to either of the philosophers whose labors we have been adverting to, it might be worth entering into such details as would more distinctly unfold their respective claims; as it is, however, I trust the short allusion made to the subject, while it places the assertions of the one in their proper light, will sufficiently vindicate the exalted merit and indisputable originality of the other.

To Mr. WATT's character, in relation to the public, and as a private individual, it is more than difficult to do justice, for the combined eloquence of the different writers who have attempted it, has only feebly depicted the influence of his talents upon the state of society; and still less has it succeeded in the more difficult portraiture of the man, occupied in the ordinary duties of life, and in the intercourse of social converse. Such, at least, is my impression, upon looking over the different biographical sketches that have lately appeared. I consider myself as highly fortunate in having occasionally enjoyed the society, and profited by the information of one who was so eminent a benefactor to his country. "He was a man," says Sir WALTER SCOTT, "whose genius discovered the means of multiplying our national resources to a degree, perhaps even beyond his own stupendous powers of calculation and combination; bringing the treasures of the abyss to the surface of the earth; giving the feeble arm of man the momentum of an Afrite; commanding manufactures to arise, as the rod of the Prophet produced water in the desert; affording the means of dispensing with that time and tide which wait for no man, and of sailing without that wind which defied the commands and threats of Xerxes himself. This potent commander of the elements, this abridger of time and space, this magician, whose cloudy machinery has produced a change on the world, the effects of which, extraordinary as they are, are perhaps only now beginning to be felt, was not only the most profound man of science, the most successful combiner of powers and calculator of numbers, as adapted to practical purposes; was not only one of the most generally well-informed, but one of the best and kindest of human beings. In his eighty-fourth year his attention was at every one's question, his information at every one's command." "No individual in his age," says another and equally able writer, "possessed more varied and exact information. He had infinite quickness of apprehension, a prodigious memory, and a certain rectifying and methodizing power of understanding, which extracted something precious out of all that was presented to it. His stores of miscellaneous knowledge were immense, and yet, less astonishing than the command he had over them. His conversation had all the charms of familiarity, with all the substantial treasures of knowledge. With this philosophical

excellence of character, be it never forgotten that Mr. WATT conjoined the higher duties and more exalted attributes of sincere, but unaffected piety. Expressing his gratitude to Providence for that length of days, and exemption from infirmity, which rendered the evening of his life cheerful and serene, he yielded up his soul in the calmest tranquillity, and passed, without pang or struggle, from the bosom of his family to that of his God !”

§ X.

It is not perfectly in chronological order to proceed in the present Section to the discoveries of Dr. PRIESTLEY*, and yet, they are so numerous and important, that it will be difficult to continue the history of chemistry up to this time, without allusion to their objects and results. I shall, therefore, endeavor to give the reader some insight into the nature and bearings of his inquiries.

PRIESTLEY’S entire force was directed upon Pneumatic Chemistry. We have seen what may be termed the materials for the foundation of this branch of knowledge, in the works of MAYOW and HOOKE; it was pursued, as we have also found, with much diligence, but, unfortunately, in rather a desultory style, by HALES; PRIESTLEY directed his attention to it with a degree of activity and skill, peculiarly his own; and, in the number of his discoveries, left his contemporaries far in the back-ground, while he certainly rivalled them in their interest and importance; and this is the more surprising, when we reflect that his philosophical studies seem generally to have been considered as subordinate to more severe and serious occupations. He first turned his attention to chemistry about 1768; he used to amuse himself with experiments on fixed air, and artificial mineral waters; and one experiment, as he says, leading to another, he soon collected those materials which he laid before the Royal Society in 1772, under the title of *Observations on different Kinds of Air*. With what zeal and success he prosecuted this subject, will be seen in the sequel.

The apparatus which is now used in the chemistry of gaseous bodies, is almost entirely of PRIESTLEY’S invention. The water-trough, with its sliding shelves and moveable supports for inverted jars; the methods of subjecting animals and plants to the action of different kinds of air; the mercurio-pneumatic apparatus for collecting gases absorbable by water; the means of measuring and weighing gases, and of subjecting them to the action of electricity, are only a few of the contrivances for which we are principally indebted to PRIESTLEY; many others, employed by MAYOW and HALES, were by him perfected or improved.

In his earliest experiments on fixed air, and on air tainted by combustion and respiration, Dr. PRIESTLEY has announced many highly interesting and new facts; but the discovery which takes precedence of the others, and upon which his fame has been chiefly, though not quite justly, founded, is that of Oxygen Gas, or, as he termed it, Dephlogisticated Air. I say not quite justly, because its brilliancy and importance have been suffered to overshadow many of his other original investigations, of

* Born at Fieldhead, near Leeds, 1733; died in Pennsylvania, 1804.

which we hear but little, though their aggregate influence upon the subsequent progress of chemistry was most direct and important; but the fact is, that PRIESTLEY having opened as it were, a new and rich mine in the science, found therein such abundance of treasure, that he was able to do little more than bring it to the surface, where it was soon pillaged and carried off.

Dephlogisticated Air was discovered by Dr. PRIESTLEY on the 1st of August, 1774; the method of experimenting which he adopted, consisted in exposing a quantity of *Red Precipitate of Mercury* to the action of the sun's rays concentrated by a burning lens; the red precipitate was contained in a small flask, filled up with quicksilver, and inverted in a basin of the same metal. "I presently found," he says, "that by means of this lens air was expelled from it very readily. Having got several times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was, that a candle burned in this air with a remarkable vigorous flame, very much like that enlarged flame with which a candle burns in nitrous air exposed to iron or liver of sulphur; but, as I got nothing like this remarkable appearance from any kind of air besides this particular modification of nitrous air, and I knew no nitrous acid was used in the preparation of the *mercurius calcinatus*, I was utterly at a loss how to account for it*." Red Lead, and several other substances, among which is enumerated *Nitre*, are also shown by our author to afford oxygen at a red heat; and here we may revert to the sagacity displayed by HOOKE, in his notions already quoted, respecting the constitution of that salt, and its nitro-aërial particles; and remind the reader how remarkably his surmises have been verified by PRIESTLEY; for upon turning to those pages of the *Micrographia*, in which the theory of combustion is explained, we cannot but admire the penetration with which the presence of a body possessing the qualities of oxygen is anticipated, though the experimental demonstration of its existence was not achieved till the middle of the succeeding century. To MAYOW we might pay a similar tribute of applause; but in canvassing the discoveries of LAVOISIER and his associates, a more favorable opportunity will offer of placing these matters in their true light.

The "nitrous air exposed to iron," alluded to in the preceding paragraph, is the gas now called Nitrous Oxide, which PRIESTLEY also discovered, though he but imperfectly investigated its properties.

The next remarkable circumstance adverted to by our author in

* The following paragraph, with which Dr. Priestley prefaces his account of the discovery of Dephlogisticated Air, presents a picture of his mind in regard to the origin of his own researches.

"The contents of this section will furnish a very striking illustration of the truth of a remark which I have more than once made in my philosophical writings, and which can hardly be too often repeated, as it tends greatly to encourage philosophical investigations; viz., that more is owing to what we call

chance, that is, philosophically speaking, to the observation of *events arising from unknown causes*, than to any proper design or preconceived *theory* in this business. This does not appear in the works of those who write *synthetically* upon these subjects, but would, I doubt not, appear very strikingly in those who are the most celebrated for their philosophical acumen, did they write *analytically* and ingenuously." (*Exp. and Obs.*, vol. ii., p. 103.)

respect to dephlogisticated air, is its action upon nitrous gas, mixed with which, "it occasioned a much more considerable diminution than atmospheric air;" and, as the fitness of air for respiration appeared connected with the absorption thus produced, it was inferred that it would support respiration, an inference which the Doctor soon verified, by placing a mouse in a jar of the dephlogisticated air, in which it lived half an hour, though, by previous trials, he knew that it would only live a quarter of an hour in the same bulk of atmospheric air.

In the observations connected with these experiments, PRIESTLEY enters pretty much at length into the theory of the production of dephlogisticated air; but I shall not follow him into these views, as they are not very consistent with facts, nor even plausibly applied to them: he hints, however, at several useful applications of oxygen, and especially recommends it for the production of intense heat, by directing a small jet of it upon a piece of burning charcoal.

Among the many and ingenious investigations of this Philosopher, none have produced more pleasing subjects of inquiry than those relating to the influence of vegetation upon air contaminated by combustion, respiration, and the putrefaction of animal matter. Finding that air was not spoiled by the growth of a sprig of mint kept in it for some months, he thought it possible that the process of vegetation might restore the air injured by burning candles; and, accordingly, on the 17th of August, 1771, he put a sprig of mint into air in which a wax candle had burned out, and, on the 27th of the same month, found that another candle burned perfectly well in it; and then, to verify the conclusion, he divided the injured air into two separate portions, putting the plant into one of them, and merely leaving the other standing over water; he never failed to find that a candle would burn in the former, but not in the latter. "This restoration of air," says PRIESTLEY, "I found depended upon the *vegetating state of the plant*: for though I kept a great number of the fresh leaves of mint in a small quantity of air in which candles had burned out, and changed them frequently for a long space of time, I could perceive no melioration in the state of the air. This remarkable effect does not depend upon anything peculiar to *mint*, for I found a quantity of this kind of air to be perfectly restored by sprigs of *balm*." Groundsel, spinach, and some other plants, were used with like effect, to show that it did not depend upon aromatic effluvia. In Dr. PRIESTLEY's *Observations on Air infected with Animal Respiration and Putrefaction*, a multitude of other facts are adduced to demonstrate its renovation when exposed to growing vegetables, and he is thus led to the following general remarks upon the subject:—"These proofs of a partial restoration of air by plants in a state of vegetation, though in a confined and unnatural situation, cannot but render it highly probable, that the injury which is continually done to the atmosphere by the respiration of such a number of animals, and the putrefaction of such masses of both vegetable and animal matter, is, in part at least, repaired by the vegetable creation; and notwithstanding the prodigious mass of air that is corrupted daily by the above-mentioned causes, yet, if we consider the immense profusion of vegetables upon the face of the earth, growing in places suited to their nature, and, consequently, at full liberty to exert all their powers, both inhaling and

exhaling, it can hardly be thought but that it may be a sufficient counter-balance to it, and that the remedy is adequate to the evil*.”

In the year 1778 Dr. PRIESTLEY resumed this investigation, and verified his main conclusions by new and satisfactory experiments; he found, however, that it was necessary for their success that the plants should be in a state of healthy and natural vegetation, and that all plants were not equally efficacious, some indeed appearing rather to deteriorate than improve the contaminated atmosphere. About this time, too, he made the capital discovery of the evolution of oxygen by aquatic plants, growing in water containing carbonic acid; that the presence of light was necessary to this change; that in sunshine it was most rapid; that it was in great measure independent of warmth; and, lastly, that the bladders of some kinds of sea-weed (*fucus vesiculosus*), often contained air purer than the atmosphere. The renovation of the air contained in water, requisite for the respiration of fishes, was thus accounted for; and the circumstance of fishes and most other aquatic animals being unable to live for any time in pure water, though exposed to air, satisfactorily explained.

By his contrivance of receiving gaseous fluids over quicksilver, PRIESTLEY was able to collect and examine a number of new aëriform products, absorbable by water; and in these inquiries he was eminently successful. CAVENDISH, in endeavouring to get inflammable air from a mixture of copper and spirit of salt, obtained one that lost its elasticity on the contact of water. “I was exceedingly desirous,” says PRIESTLEY, “to become acquainted with it, and therefore began by making the experiment in quicksilver, which I never failed to do in any case when I suspected that air might either be absorbed by water, or in any other manner affected by it: and, by this means, I presently got a much more distinct idea of the nature and effects of this curious solution.” He then goes on to show that this singular gas is derived from the acid, that it is very absorbable by water, and that common Spirit of Salt is in fact an aqueous solution of it. His next discovery in this department, was that of an *alkaline air* from a mixture of lime and sal-ammoniac; it also was absorbed by water, forming “volatile spirit of sal-ammoniac, much stronger than that procured by any other means.” He now thought that by adding the acid to the alkaline air, he might possibly produce a neutral air, but immediate condensation ensued, and *sal-ammoniac* was deposited. What is now termed Sulphurous Acid, (or by PRIESTLEY Vitriolic Acid Air,) he also discovered; he obtained it in various ways, but chiefly by heating mercury with oil of vitriol; he examined many of its combinations, and inquired into its action upon a variety of bodies†.

* PRIESTLEY on *Air*, vol. i. p. 93, 3rd edition, 1781.

† The notice of this discovery enables me, by the insertion of the following extract from his *History of Vitriolic Acid Air*, to show the candour and exactness with which he acknowledges the hints, assistance, and discoveries of others:—

“My first scheme was to endeavour to get the vitriolic acid in the form of

air, thinking that it would probably be easy to confine it by quicksilver, for, as to the nitrous acid, its affinity with quicksilver is so great that I despaired of being able to confine it to any purpose. I, therefore, wrote to my friend Mr. Lane to procure me a quantity of volatile vitriolic acid,” &c. “Seeing Mr. Lane the winter following, he told me, that if I would only heat any oily or greasy

I have now enumerated the principal discoveries which PRIESTLEY may claim as original; and, in importance, they are second to none that had been previously made, and barely inferior to those that have adorned the later progress of Chemistry. We can scarcely call him the *founder* of Pneumatic Chemistry, after perusing the works of HALES and BLACK; but he achieved more in that new department of the science, than any of his predecessors or contemporaries; and though on some points anticipated, his claims to originality, are on others, quite unequivocal. He cannot be called the *discoverer* of Nitrous Gas, for it is noticed by MAYOW; yet he developed its principal properties, pointed out its useful eudiometrical applications, and showed many new modes of obtaining it. He has been stigmatized as a defender of the unintelligible system of phlogiston; and he did defend it with unpardonable pertinacity*; but when we reflect, that equally erroneous theories have been as warmly espoused in our own

matter with oil of vitriol, I should certainly make the very thing I wanted, viz., the volatile or sulphureous vitriolic acid; and, accordingly I meant to have proceeded upon this hint, but was prevented from pursuing it by a variety of engagements.

“Some time after this, I was in company with Lord Shelburne, at the seat of Mons. Trudaine, at Montigny, in France; where, with that generous and liberal spirit by which that nobleman is distinguished, he has a complete apparatus of philosophical instruments, with every other convenience and assistance for pursuing such philosophical inquiries as any of his numerous guests shall choose to entertain themselves with. In this agreeable retreat, I met with that eminent philosopher and chemist, Monsieur Montigni, Member of the Royal Academy of Sciences; and conversing with him upon the subject, he proposed our trying to convert oil of vitriol into vapour, by boiling it on a pan of charcoal in a cracked phial. This scheme not answering our purpose, he next proposed heating it together with oil of turpentine. Accordingly, we went to work upon it, and soon produced some kind of air, confined with quicksilver; but our recipient being overturned by the suddenness of the production of the air, we were not able to catch any more than the first produce, which was little else than the common air which had lodged on the surface of the liquor, and which appeared to be a little phlogisticated by its not being much affected by a mixture of nitrous air.”

* Dr. Priestley's last publication is a tract, which appeared after his retirement to America, in 1800. It is entitled *The Doctrine of Phlogiston established, and*

that of the Composition of Water refuted.

It contains a variety of miscellaneous observations on the phlogistic and anti-phlogistic theories; but it would be useless to follow the author into his unsubstantial speculations on these subjects. He has, however, thrown out some important considerations relating to his claims of originality as the discoverer of dephlogisticated air. The following paragraph appears of sufficient interest to be transcribed:—“Now that I am on the subject of the *right of discoveries*, I will, as the Spaniards say, leave no ink of this kind in my inkhorn; hoping it will be the last time that I shall have any occasion to trouble the public about it. M. Lavoisier says (*Elements of Chemistry, English translation*, p. 36), ‘this species of air (meaning dephlogisticated) was discovered almost at the same time by Mr. Priestley, Mr. Scheele, and myself.’ The case was this:—Having made the discovery some time before I was in Paris in 1774, I mentioned it at the table of M. Lavoisier, when most of the philosophical people in the city were present; saying, that it was a kind of air in which a candle burned much better than in common air, but I had not then given it any name. At this all the company, and M. and Madame Lavoisier as much as any, expressed great surprise; I told them I had gotten it from *precipitate per se*, and also from *red lead*. Speaking French very imperfectly, and being little acquainted with the terms of chemistry, I said *plomb rouge*, which was not understood, till M. Macquer said, ‘I must mean *minium*.’ Mr. Scheele's discovery was certainly independent of mine, though I believe not made quite so early.” P. 88.

days, by men who in no respect are to be considered as inferior to our author, we must not impeach his discernment, upon so flimsy an accusation. When we consider his numerous, and as it were, incompatible occupations; and remember the many channels into which his exertions were occasionally directed, we presently detect the source of that wavering of opinion, and unsteadiness of research, which his philosophical pursuits display. His experiments were almost always submitted to the public in a crude and undigested form, for he had no time to build them into theories, or to concoct them into generalizations; and it is perhaps as well that he had not, for the bent of his mind was evidently such, as to shine in experiment rather than argument.

The *constitution of the atmosphere* was one of the many inquiries which engaged PRIESTLEY's diligence*. In 1772, Dr. RUTHERFORD demonstrated the existence of a peculiar elastic fluid in atmospheric air, differing from fixed or mephitic air, and yet, like it, extinguishing flame, and unfit for respiration†. This component part of the atmosphere was, by PRIESTLEY, called *Phlogisticated Air*: and he showed that when mixed with nitrous gas, it suffered no diminution; but, on the contrary, that dephlogisticated air, on the same admixture in due proportions, was almost entirely absorbed over water; hence the method before noticed which he introduced, of ascertaining what was termed the goodness of atmospheric air, by the degree of absorption exhibited upon a certain admixture of nitrous gas, over water.

It was for his various discoveries, and more especially those relating to the physiology of vegetation, that the Council of the Royal Society honored Dr. PRIESTLEY by the presentation of Sir GODFREY COPLEY's medal, on the 30th of November, 1783‡.

* The ancients appear to have regarded air as an ultimate principle of matter. Thus Lucretius,—

Aera nunc igitur dicam, quid corpore toto
Innumerabiliter privis mutatur in horas;
Semper enim, quodquomque fluit de rebus, id omne
Aeris in magnum fertur mare, qui nisi contra
Corpora retribuatur rebus, recreeturque fluentis,
Omnia, jam resoluta forent, et in aera versa.
Haud igitur cessat gigni de rebus, et in res
Recidere assidue, quoniam fluere omnia constat.
De Rerum Natura, Lib. V. v. 274.

† “Sed Aer salubris et purus, non modo respiratione animali ex parte fit mephiticus, sed et aliam indolis suæ mutationem inde patitur. Postquam enim omnis aer mephiticus ex eo, ope lixivii caustici secretus et abductus fuerit, qui tamen restat, nullo modo salubrior inde evadit, nam quamvis nullam ex aqua calcis præcipitationem faciet, haud minus quam antea, flammam et vitam extinguit.”

‡ Sir Godfrey Copley originally bequeathed five guineas to be given at each anniversary meeting of the Royal Society, by the determination of the President and Council, to the person who had been the author of the best paper of

experimental observation for the year past. In process of time, this pecuniary reward, which could never be an important consideration to a man of enlarged and philosophical mind, however narrow his circumstances might be, was changed into the more liberal form of a gold medal, in which form it is become a truly honourable mark of distinction, and a just and laudable object of ambition. It was, no doubt, always usual with the Presidents, on the delivery of the medal, to pay some compliment to the gentleman on whom it was bestowed; but the custom of making a set speech on the occasion, and of entering into the history of that part of philosophy to which the experiment related, was first introduced by Mr. Martin Folkes. The discourses, however, which he and his successors delivered, were very short, and were only inserted in the minute-books of the Society; none of them had ever been printed before Sir John Pringle was raised to the chair of the Society.—CHALMERS's *Biographical Dictionary*.—*Life of PRINGLE*.

Sir JOHN PRINGLE, who was then President, delivered on this occasion an appropriate discourse upon the different kinds of air, in which, after expatiating upon the discoveries of his predecessors, he points out the especial merits of PRIESTLEY'S investigations. In allusion to the purification of a tainted atmosphere by the growth of plants, the President has thus expressed himself:—

“From these discoveries we are assured that no vegetable grows in vain; but that, from the oak of the forest to the grass of the field, every individual plant is serviceable to mankind; if not always distinguished by some private virtue, yet making a part of the whole which cleanses and purifies our atmosphere. In this, the fragrant rose and deadly nightshade co-operate; nor is the herbage, nor the woods that flourish in the most remote and unpeopled regions, unprofitable to us, nor we to them, considering how constantly the winds convey to them our vitiated air, for our relief and their nourishment. And if ever these salutary gales rise to storms and hurricanes, let us still trace and revere the ways of a beneficent Being, who not fortuitously, but with design, not in wrath, but in mercy, thus shakes the water and the air together, to bury in the deep those putrid and pestilential effluvia which the vegetables on the face of the earth had been insufficient to consume*.”

The chemistry of gaseous bodies, in consequence chiefly of PRIESTLEY'S investigations, now became a main branch of the science, and some of his most eminent contemporaries were equally diligent with himself in its promotion and elucidation. Among others, BERGMAN and his friend and pupil, SCHEELÉ, may be ranked among its successful followers; and CAVENDISH lent it his powerful aid; but I have thought it better to confine myself to the abstract view of such of PRIESTLEY'S discoveries as may

* Dr. Franklin, in a letter upon the subject of these discoveries to Dr. Priestley, has expressed himself as follows:—

“That the vegetable creation should restore the air which is spoiled by the animal part of it, looks like a rational system, and seems to be of a piece with the rest. Thus, fire purifies water all the world over. It purifies it by distillation, when it raises it in vapor and lets it fall in rain; and further still by filtration, when keeping it fluid, it suffers that rain to percolate the earth. We knew before, that putrid animal substances were converted into sweet vegetables, when mixed with the earth and applied as manure; and now, it seems that the same putrid substances, mixed with the air, have a similar effect. The strong thriving state of your mint, in putrid air, seems to show that the air is mended by taking something from it, and not by adding to it. I hope this will give some check to the rage of destroying trees that grow near houses,

which has accompanied our late improvements in gardening, from an opinion of their being unwholesome. I am certain, from long observation, that there is nothing unhealthy in the air of woods; for we Americans have everywhere our country habitations in the midst of woods, and no people on earth enjoy better health, or are more prolific.”—*Phil. Trans.* 1772, page 199.

Nothwithstanding these researches, which have exposed some very curious facts relative to the chemical physiology of plants, it has been surmised that the causes of the renovation and equality of our atmosphere are not yet entirely ascertained; for, although growing vegetables, under the influence of light, purify the air (by the absorption of carbon and the evolution of oxygen), yet, when in blossom, and when in a state of decay, they add to its contamination. There seems, however, no reason to doubt that vegetation is adequate to the decomposition of the whole of the carbonic acid which is thrown into the atmosphere.

be strictly termed his own, than to blend them with the achievements of other philosophers, who experimented with distinct views, though occasionally treading in his footsteps.

§ XI.

BERGMAN, of Sweden, was born in the year 1735, and died in 1784, in consequence of too intense application to his studies: he was not only a diligent traveller in the beaten paths of Chemistry, but he searched the depths, and ascended the heights of the science; his life was short, but as he neither lost nor misemployed time, his activity compensated for the brevity of his days; he not only opened a new mine in his favorite science, but examined its treasures and scattered its riches, for BERGMAN may be said to have almost invented the art of chemical analysis.

In his *Prefatory Essay on the Investigation of Truth*, this author has depicted his feelings upon the subject of experimental science, in perspicuous and unaffected terms; and a mind so directed, could not but be successful in its exploits, when we remember, that even in his days, there were few willing entirely to throw off the presumption of scholastic philosophy. "A tendency," he says, "to Cartesianism still exists, and upon attentive consideration it will not appear wonderful that the human mind should delight to indulge in this method; for, on the one hand, the way of experiment is expensive, troublesome, and tedious; all minds, therefore, are not capable of enduring it; many are without the proper instruments, others want the necessary dexterity; but the most universal defect is that of patience and perseverance, so that if the experiment does not at once succeed, it is abandoned in disgust. Man, in his ordinary state, seems by nature prone to indolence. On the other hand, the contemplative method favours the desire of knowledge; by pretending to unlock the secrets of nature with ease and expedition, it soothes the natural rage of explaining all things; and by supposing everything accessible to the human intellect, administers pleasing flattery to vanity and arrogance."

It is upon the talents of BERGMAN, as an *analyst*, that I propose to dwell; it is there that he was pre-eminently original and successful; and upon that foundation, his character as a chemist may safely be built.

The use of *tests*, for the discovery of certain substances held in aqueous and other solutions, is first particularly dwelt upon by BOYLE, and he was sometimes very fortunate in their contrivance and application. He noticed the conversion of certain vegetable blues to red by acids, and to green by alkalis; the cloudiness produced by common salt in solution of silver, its discoloration by liver of sulphur, and several other circumstances connected with the detection of certain principles by chemical re-agents. In 1667 DU CLOS undertook an examination of the waters of France; and in 1686 HIERNE published some clever experiments upon the same subject, in Sweden. In these writers, the use of galls for the detection of iron is alluded to, and the necessity pointed out of examining the residuary product of evaporation. In 1726 and 1729 BOULDUC used spirit of wine to precipitate certain saline bodies insoluble in that menstruum. In 1755 VENEL pointed out the existence of fixed

air in the waters of Seltzer, Spa, and Pyrmont; LANE, in 1769*, showed the method of imitating chalybeate springs; and in 1772 Dr. PRIESTLEY published directions for saturating water with fixed air.

BERGMAN, in his *Essay on Mineral Waters*, after adverting to a variety of circumstances relating to their general characters and sources, proceeds to point out, in the seventh section, the principal *re-agents* and *precipitants* useful in their examination, and to describe the nature of their changes and indications, with useful precision, in the following order:—
 A. Infusion of litmus, or turnsole, is so delicate a test for the acids, that a single grain of sulphuric acid reddens 408 cubic inches of the blue tincture. Paper, dipped in this tincture, and reddened by distilled vinegar, has its blue color restored by alkalis; but the tincture is more sensible than the paper, for the latter is not reddened by aërial acid (fixed air); yet one part of water, saturated with aërial acid, renders fifty parts of the infusion red. B. Tincture of Brazil-wood becomes blue by alkalis, and is sensible to less than one grain of crystallized soda in 4000 of water. C. Turmeric, either on paper, or in watery tincture, is a good, but less sensible, test for alkalis, which render it brown. D. Tincture of galls discovers iron by a purple or black cloud. E. Prussiate of Potash produces a blue tinge in water containing a minute portion of iron; it also precipitates other metals; copper, brown; manganese, white. F. Sulphuric acid forms a white precipitate in all solutions containing baryta. If it produce bubbles, it indicates some combination of aërial acid. Nitric acid is highly useful for showing the presence of sulphur, which it precipitates from hepatic waters. G. Oxalic acid detects the minutest quantity of lime, by producing a white cloud, either immediately, or after some hours. This test shows that scarcely any water is free from lime; and the purest, within twenty-four hours, deposits a portion of oxalate of lime, although sometimes so sparingly as to escape observation, unless lines be drawn on the bottom of the vessel with a glass rod, in the direction of which the precipitate attaches itself. H. Aërated fixed alkali throws down the metals and earths; if the substance be easily soluble in aërial acid, the caustic alkali may be used. I. Aërated volatile alkali also throws down earths and metals, and is an excellent test for the presence of copper, which it indicates by a blue color, more or less intense according to the quantity of alkali added. K. Lime-water detects aërial acid, by a precipitate of aërated lime. L. Muriate of baryta forms an insoluble white precipitate in water containing any soluble vitriolic salt; twelve grains of crystallized Glauber's salt, dissolved in a kanne of distilled water (about three quarts), immediately exhibits white striæ on the application of this test. Even one grain in the kanne exhibits a white cloud after some hours; and as it only contains 0·26 grains of

* Mr. Lane was the first who ascertained the solubility of iron in water impregnated with fixed air.—*Phil. Trans.* 1769. "By this means," says Sir John Pringle, in his discourse on the different kinds of air, delivered at the anniversary meeting of the Royal Society, November 30, 1773, "the nature of the metallic

principle in mineral waters was clearly explained, and the whole analysis of those celebrated fountains, so often attempted by chemists and others, and still eluding their laboured researches, was thus, in the most simple manner, brought to light."

sulphuric acid, we may judge of the nicety of this precipitant, which even exceeds turnsole itself in sensibility. M. Muriate of lime may be used for the detection of fixed alkali, but it is an ambiguous test, because, if sulphate of magnesia be present, it produces gypsum. N. Solution of alum is also of little use, though occasionally employed as a test for alkalis. O. Nitrate of silver is a certain and delicate indicator of muriatic acid and its combinations. A grain of common salt, in a kanne of water, is instantly rendered evident by white streaks. Under some circumstances it may also form a precipitate with sulphuric acid, but sulphate of silver is much more soluble than muriate; thus, no visible turbidness arises, unless the kanne of water contains ninety-eight grains of Glauber's salt, or twenty-five of vitriolic acid. The presence of hepatic air renders the precipitate of silver more or less brown. Alkalis, lime, and magnesia, also precipitate nitrate of silver. P. Nitrate of mercury is a prevaricating test, but very sensible to a variety of substances that may exist in mineral waters. As BERGMAN has not pointed out any particular application, in which this salt is essential, it will not be necessary to follow up his remarks on it, though in other respects important. Q. Corrosive sublimate; R. Acetate of lead; S. Sulphate of iron; and T. White arsenic, are enumerated, but their utility is dubious, and the observations upon them of little value to the analyst. U. Spirituous solution of soap is useful in giving general indications of the purity of water, which, if pure, scarcely renders it opalescent; but, if abounding in foreign materials, or *hard*, and unfit for washing, it produces more or less opacity or precipitation. X. Liver of sulphur is affected by so many causes, that it may be dispensed with in the examination of waters. Y. Alcohol throws down such salts as it cannot dissolve, especially the sulphates. It dissolves many muriates and nitrates.

I have thus enumerated the tests recommended by BERGMAN, and given an abridged account of his remarks upon them, for the purpose of showing the progress which, under his assistance, was made in Analytical Chemistry: it is true that of many of these re-agents, and of their applications, he was not the original inventor; but he was the first who showed the real value and limits of the indications which they afford; an effort of no common sagacity, when we revert to the state of chemistry in his time.

Proceeding with the analysis of mineral waters, BERGMAN next adverts to the gaseous contents, which may be expelled by heating a given portion of the water in a retort, the beak of which is plunged into the mercurio pneumatic apparatus, and the gas secured in the usual way. It commonly consists of pure air and aerial acid; the latter may be absorbed by lime-water. The presence of hepatic air is easily recognised by its odor. The remaining water is directed to be evaporated to dryness, and the residue weighed, and digested in pure alcohol; the residue, insoluble in alcohol, is then to be shaken with eight parts of cold water; and finally, the matters which resist the action of alcohol and cold water are to be boiled in four or five hundred parts of distilled water, and the solution filtered. The ultimate residuum generally contains iron and carbonate of lime, or perhaps of magnesia, previously suspended by

carbonic acid; it may be in a few instances argillaceous or silicious, and perhaps contains manganese; and directions are given at length for its separate analysis, as well as that of the aqueous and alcoholic solutions. It is here that BERGMAN displays an ingenuity and accuracy then new to chemical science; for, in measuring his merits by a true estimate, we must go back to the state of Chemistry at his time, and divest ourselves of its modern perfections and refinements; then, the peculiar and genuine character of his researches will become prominent.

Having, in the paper of which the above is an outline, described the general principles of the analysis of mineral waters, BERGMAN proceeds, in several following essays, to apply them to individual analyses; and his dissertations on the waters and acidulous spring of Upsal, on sea-water, and on the artificial preparation of hot and cold medicated waters, each exhibit proofs of his skill as an analyst, and accuracy as an experimenter; but, although these, and his other detached essays, are excellent in their way, we must here pass them by, in order to examine such of his contributions as tended to the general improvement and extension of chemical science; among these, his luminous dissertation on Chemical Attraction*, already adverted to, is pre-eminent; and the twenty-fourth essay in the second volume of his *Opuscula*, entitled *De Minerarum Docimasia Humida* (on the Art of Assaying in the Humid Way,) must be considered as the parent source of that branch of analytical chemistry, so successfully followed up, though upon a limited scale, by SCHEELÉ, and in the improvement and extension of which KLAPROTH passed his long and laborious life.

It must be premised, that the *assay*, or analysis of minerals, had, with the exception of the experiments of MARGRAAF†, hitherto been confined to certain operations effected by the aid of fire, in which, except in

* *De Precipitatis Metallicis.*

† Among those whose names became eminent in the history of chemical science during the first half of the eighteenth century, Margraaf is entitled to particular mention. He was born at Berlin, in 1709, where he died in 1782. He was a pupil of the once-celebrated Neumann, a man whose works are now not much thought of, but who did considerable service to the chemistry of his day. Caspar Neumann was born at Zullichau, in Prussia, in 1682; and in 1705 we find him enjoying the patronage of the King of Prussia, by whom he was sent to complete his studies at the University of Halle. In 1711 he became a pupil of Boerhaave, and shortly after visited England, whence he accompanied George I. to Hanover, in 1716. In 1723 he became Professor of Practical Chemistry in the Royal College of Berlin, where he died in 1737. His works consist chiefly in dissertations on various subjects of chemical inquiry, published in the *Transactions of the Royal Society*,

and in the *Miscellanea Berolinensia*. His Lectures were not printed till after his death, and proved a valuable magazine of chemical knowledge. "The author," says Dr. Lewis, who edited his works, "biassed by no theory, and attached to no opinions, has inquired by experiment into the proportions and uses of the most considerable natural and artificial productions, and the preparations of the principal commodities which depend on chemistry, and seems to have candidly and without reserve communicated all he discovered."

In 1733, Margraaf pursued chemistry under Juncker, at Halle, and, having returned to Berlin, in 1738, we find several of his contributions in the *Transactions of the Scientific Society*, of that capital. Subsequent to that period his works were collected and published at Paris in 1762. They contain a great body of information, at that time novel and important, but they are chiefly entitled to notice, as furnishing specimens of the art of analysis.

common and obvious cases, their nature was rather guessed at than demonstrated. This art had its origin in the sixteenth century; and in 1576 the celebrated work of AGRICOLA brought before the public all that was important in relation to it, describing the instruments and processes with scrupulous and minute accuracy, and illustrating them by a curious collection of cuts. AGRICOLA was succeeded by LAZARUS ERCKERN, whose work on the docimastic art is much eulogized by BOERHAAVE. In the above-named essay, BERGMAN points out the fallacies and imperfections to which igneous analysis is liable, and dwells upon the advantage of operating in the humid way, that is, by solvents and precipitants. He then proceeds to separate examinations of various metallic ores, as illustrations of his new method. Many of the conclusions and reasonings contained in this essay, are founded upon the details of the preceding one, on Metallic Precipitates. "He," says our author, "who first saw the corrosion of a metal by a limpid liquid, who beheld the opaque and ponderous body gradually disappear, and become a part of a transparent and apparently homogeneous fluid, and who saw the same metal reappear upon the addition of a proper precipitant, must have been infinitely surprised, and struck with admiration of the occult powers of nature. But because we are accustomed to these phenomena, we neglect inquiring into their causes, though of the utmost importance, as forming the entire basis of practical chemistry. Such phenomena are so varied and intricate that volumes would be insufficient for their complete discussion; so that I propose to limit my observations to the separation of metals from acids, and to the particular consideration of *the weights of the precipitates*." Then, after a luminous summary of the general phenomena of the solution of metals, he advances a series of facts relating to their precipitation; he shows that the caustic fixed alkalis occasion precipitates of the *calces*, but loaded with water, by which their weight is much increased: that carbonated alkali precipitates carbonated oxides, by double decomposition: that certain acids, which form insoluble compounds with metals, throw them down from their soluble compounds: that certain salts act in the same way, by double elective attraction; and that in some cases triple combinations ensue, as when platinum is precipitated by sal ammoniac. He then adverts to the decomposition of one metallic salt by another, even where the acid is the same in both. Thus, sulphate of iron and muriate of tin decompose muriate of gold. The metals also precipitate one another after a certain order, which is the same in all acid solvents, and effected by double elective attraction, "for the metal to be precipitated exists in the solution in a calcined state; but, being reduced by the phlogiston of the precipitant, falls to the bottom; while the precipitant, being calcined, becomes soluble. Although," he says, "many anomalous circumstances occur in this matter, the order is constant, and never inverted." The fifth section of this paper explains the use of tests for discriminating the metals, pointing out the colors of metallic precipitates. "Gold and platinum are only in part separated from acids by the alkalis. Nitrate of silver affords a brown precipitate with caustic, and a white with aërated soda, and with muriatic acid. Solution of nitrate of mercury gives a red precipitate with carbonated, and a yellowish, or orange, with caustic alkali. The latter is black, if the solution be prepared

without heat. Nitrate of lead is precipitated, white by caustic alkali, an excess of which re-dissolves the precipitate. Nitrate of copper gives a bright-green compound with aërated, and brown with phlogisticated alkali (prussiate of potash). Iron is thrown down green by aërated alkali, and the precipitate, on exsiccation, becomes brownish-yellow. Tin gives a white cloud with all the alkalis; bismuth, white with water and alkalis; nickel, greenish-white with alkalis and prussiate of potash; zinc and antimony, white with all alkalis."

Such is a short abstract of the contents of this section, which, although obscured by the language of the old school, and therefore scarcely, perhaps, intelligible to the chemical student of the present day, abounds in useful and perspicuous details: it is followed by the concluding section, containing a table of the relative weights of precipitates, procured in different ways, from a solution of one hundred parts of metals; and, as BERGMAN observes, "this table, upon proper examination, reveals many mysteries." It seems to have been the general opinion at this period, that the relative weights of precipitates were in all cases the same; that is, one hundred parts of lead, for instance, dissolved by nitric acid, and precipitated by caustic, aërated, and phlogisticated alkali, and by sulphuric acid, would furnish an equal weight of precipitate in each individual instance. Our author has shown the fallacy of this opinion; and demonstrates the difference of weights to depend upon the different proportions of the precipitant contained in the precipitate, and upon the occasional retention of a portion of the solvent. The list of precipitates annexed to this paper, will disclose, to the attentive observer, principles analogous to those exhibited by the tables of RICHTER, and upon which one of the main pillars of the theory of definite proportions may be said to rest.

BERGMAN's essay on fixed air, or as he calls it, *aërial acid*, is the last of which I shall make any particular mention. His chief experiments on this subject were probably made about the year 1770. The dissertation I am now quoting was read, in 1774, before the Royal Society of Sciences at Upsal, and is printed in their *Transactions* for 1775. After describing the several methods of obtaining fixed air, by the action of acids upon carbonates, by submitting them to a red heat, and by fermentation, he proceeds to define the meaning of the word *acid*, in order to show that fixed air belongs to that class of bodies; that it is soluble in water, that it has a sour taste, reddens turnsole, and unites to, and forms crystallizable compounds with alkalis, destroying at the same time their causticity. He detected this acid in the *marmor metallicum* of CRONSTEDT (carbonate of baryta), and observed the rapidity with which baryta-water absorbs carbonic acid from the air, forming an effervescent precipitate. Speaking of the action of carbonic acid upon lime, he gives a masterly sketch of the principal facts relating to the composition and decomposition of the carbonate of lime: he shows the solubility of calcareous spar in water impregnated with fixed air, and its subsequent deposition, often in small crystals; and the same property is also proved to belong to magnesia. BERGMAN then goes on to discuss the elective attractions of fixed air, of which he gives the following table:—

He says it appears to be the weakest acid known, for it is expelled not only by vinegar, but by the phlogisticated acids of nitre and of vitriol (nitrous and sulphurous acids); yet he observes that acetate of lead is decomposed by carbonic acid, which appears an anomaly, and suggests a question which he leaves undecided till experiment shall have enabled him to explain it. The acid properties of fixed air are next dwelt upon, and the probability of its acidity resulting from foreign matter negatived; for when "rightly depurated, though extricated by the most different means from the most different materials, whether by fire or by solution, it is nevertheless always the same, and always acid. I conclude, therefore, with all the certainty attainable in physics, that acidity is a property essential to that elastic fluid." From the imperfection of apparatus, BERGMAN erred a good deal in calculating the specific gravity of fixed air; he, however, proved it heavier than atmospheric air, and thence accounts for its lodging in low situations, as in pits and grotts: it is also shown to extinguish flame.

AERIAL ACID.

Pure terra ponderosa.
 — lime.
 — fixed vegetable alkali.
 — fixed mineral alkali.
 — magnesia.
 — volatile alkali.
 — Zinc.
 — Manganese.
 — Iron.

The essays which I have now quoted, and which may be taken as a fair sample of his method of investigation, exhibit BERGMAN in the light of a true philosopher, employing hypothesis as the precursor, and not the substitute of experiment; countenancing no theory but such as admits of rigid demonstration; advancing no favorite doctrines nor hasty speculations; but always the candid narrator of facts. As the repeater of the experiments of others, he measures and weighs their conclusions, and assigns them their proper place in the history of science. When in the character of an original inquirer, he kindles the torch of experiment, and never advances beyond the boundary of its light. He seems profoundly to have admired Newton, and to have endeavoured to transfuse his methods of investigation into chemistry. "That illustrious personage," he says, "having solicitously accumulated facts, examined them with accuracy, and compared them with acuteness; from effects he advances to causes, and thence deduces the laws of the creation. His progress, though slow, is certain; and his method, though tedious, is continually unveiling the mysteries of nature. An edifice thus constructed acquires firmness by elevation, for its foundations are solid and permanent."

There is more method in BERGMAN than in any antecedent chemical writer; his researches appear always to have been made with an object in view; and there is an unity of design in his philosophical papers, which pleasingly distinguishes them from the undigested chaos of experiments and observations which we are obliged to wade through in many preceding authors.

BERGMAN had many celebrated successors in analytical chemistry, as applied to mineral substances; among these, KLAPROTH and VAUQUELIN have especially contributed to the progress of this branch of the science. MARTIN HENRY KLAPROTH, was born at Wernigerode, in Prussia, on the 1st of December, 1743; and died at Berlin on the 1st of January, 1817.

He was an excellent man, and a diligent and accurate analyst; he was a pupil of ROSE of Berlin, who died in 1771. He published a variety of important papers in periodical [works; and in 1795 collected them, under the title of *Beiträge zur Chemischer Kenntniss der Mineralkörper*, (contributions towards the chemical knowledge of mineral substances.) Of this work, consisting of six volumes, the last was published in 1815; it contains no less than two hundred and seven essays*.

VAUQUELIN, who died, at an advanced age in Paris, in 1829, was originally a peasant boy of Normandy. He was employed in Fourcroy's laboratory, where he not only acquired great dexterity in the ordinary duties of his situation, but became an expert and original analyst; he afterwards rose to high eminence in his profession, and his numerous and important contributions and discoveries are lasting monuments of his skill and industry.

Among the mineral analysts and improvers of analytical chemistry in this country, CHENEVIX deserves honourable mention. The following brief account of his contributions, and of the curious and mysterious controversy respecting Palladium, in which he was at one time involved, I copy from Dr. THOMSON'S *History of Chemistry*, vol. ii., p. 215.

"Mr. Chenevix deserves also to be mentioned as an improver of analytical chemistry. He was an Irish gentleman, who happened to be in Paris during the reign of terror, and was thrown into prison, and put into the same apartment with several French chemists, whose whole conversation turned upon chemical subjects. He caught the infection, and, after getting out of prison, began to study the subject with much energy and success, and soon distinguished himself as an analytical chemist. His analysis of corundum and sapphire, and his observations on the affinity between magnesia and silica, are valuable, and led to considerable improvements in the method of analysis. His analyses of the arseniates of copper, though he demonstrated that several different species exist, are not so much to be depended on; because his method of separating and estimating the quantity of arsenic acid is not good. This difficult branch of analysis was not fully understood till afterwards. Chenevix was for several years a most laborious and meritorious chemical experimenter. It is much to be regretted that he should have been induced, in consequence of the mistake into which he fell respecting palladium, to abandon chemistry altogether. Palladium was originally made known to the public by an anonymous handbill which was circulated in London, announcing that *palladium*, or new silver, was on sale at Mrs. Forster's, and describing its properties. Chenevix, in consequence of the unusual way in which the discovery was announced, naturally considered it as an imposition on the public. He went to Mrs. Forster's, and purchased the whole palladium in her possession, and set about examining it, prepossessed with the idea that it was an alloy of some two known metals. After a laborious

* Professor Frederick Stromeyer of Göttingen, who died in 1835, was a chemist of most distinguished analytical attainments, and deserves to be especially mentioned as one of the successful followers of the methods chalked out by Klaproth. He was Inspector-general of

the Apothecaries for the Kingdom of Hanover; and it was in discharging the duties of that office that he was led to notice certain peculiarities in the oxide of zinc, prepared for pharmaceutical uses: his further inquiries on this subject terminated in the discovery of *cadmium*.

set of experiments, he considered that he had ascertained it to be a compound of platinum and mercury, or an amalgam of platinum made in a peculiar way, which he describes. This paper was read at a meeting of the Royal Society by Dr. Wollaston, who was Secretary, and afterwards published in their *Transactions*. Soon after this publication, another handbill was circulated, offering a considerable price for every grain of palladium *made* by Mr. Chevenix's process, or by any other process whatever. No person appearing to claim the money thus offered, Dr. Wollaston, about a year after, in a paper read to the Royal Society, acknowledged himself to have been the discoverer of palladium, and related the process by which he had obtained it from the solution of crude platina in aqua regia. There could be no doubt after this, that palladium was a peculiar metal, and that Chenevix, in his experiments, had fallen into some mistake, probably by inadvertently employing a solution of palladium, instead of a solution of his amalgam of platinum; and thus giving the properties of the one solution to the other. It is very much to be regretted that Dr. Wollaston allowed Mr. Chenevix's paper to be printed, without informing him, in the first place, of the true history of palladium; and I think that if he had been aware of the bad consequences that were to follow, and that it would ultimately occasion the loss of Mr. Chenevix to the science, he would have acted in a different manner. I have more than once conversed with Dr. Wollaston on the subject, and he assured me that he did everything that he could do, short of betraying his secret, to prevent Mr. Chenevix from publishing his paper; that he had called upon, and assured him, that he himself had attempted his process without being able to succeed, and that he was satisfied that he had fallen into some mistake. As Mr. Chenevix still persisted in his conviction of the accuracy of his own experiments after repeated warnings, perhaps it is not very surprising that Dr. Wollaston allowed him to publish his paper; though, had he been aware of the consequences to their full extent, I am persuaded that he would not have done so. It comes to be a question whether, had Dr. Wollaston informed him of the whole secret, Mr. Chenevix would have been convinced."

The Honourable EDWARD HOWARD also deserves a place among those eminent for their contributions to analytical chemistry. He was the first who accurately examined meteoric stones, and showed their identity from various places. (*Phil. Trans.*, 1802.)

§ XII.

BERGMAN was followed by two great and contemporary luminaries of chemical science, CAVENDISH*, and SCHEELE; and though each attained distinction, they reached it by very different roads; showing the little influence of external circumstances upon the growth of inherent genius. The former was a leading person in the scientific circles of London; of noble family, and princely affluence. The latter, of humble origin and with limited means, made up for the deficiencies of place and fortune by zeal and economy, and, in the retirement of a Swedish village, raised a reputation that soon extended itself over Europe. In private life,

* Born in London, 1731; died at Clapham, 1810.

CAVENDISH was unambitious, unassuming, bashful, and reserved; he was peevishly impatient of the inconveniences of eminence; he detested flattery, and was uneasy under merited praise: he therefore shunned general society, and was only familiar in a very limited circle of friends. He was in the habit of dining every Thursday at the Royal Society Club, and there he always bore his faculties meekly; his conversation was varied and instructive; upon all subjects of science he was at once luminous and profound; and in discussion, wonderfully acute.

Mr. CAVENDISH made two capital discoveries; one of which, that of the composition of nitric acid, has already been adverted to, and arose out of his researches on hydrogen, and on the products of its combustion, which terminated in ascertaining the composition of water. His first communication to the Royal Society relates to the analysis of the waters of Rathbone Place, and contains nothing worthy of particular notice. In 1776, he presented the same learned body with a dissertation on Inflammable, Fixed, and Nitrous Air, printed in the *Philosophical Transactions* for the same year, and full of important and original matter. Though his observations on fixed and on nitrous air were highly valuable, he had here been anticipated in some respects, and contemporary chemists were on most points his successful rivals; but his investigations relating to the properties of hydrogen were entirely his own; for, although it was known to others that that gas was generated by the action of certain acids on certain metals; though MAYOW had collected it, and HALES proved its combustibility; it may safely be asserted, that the phenomena of its production had entirely escaped attention, and that its principal properties were previously unknown. CAVENDISH shows that different metals afford different quantities of hydrogen; thus zinc yielded more than iron, and iron more than tin; and further, that the state of dilution and quantity of the acid, provided there was enough to dissolve the metal, did not affect either the quantity or quality of the air. In examining its properties, our author observed that it extinguished flame, destroyed animal life, and burned, when pure, with a pale blue flame: he determined its specific gravity, and found it was the lightest of all ponderable matter; hence its subsequent suggestion by Dr. BLACK, and Mr. CAVALLO, as a substitute for rarefied air, in the balloon: the former indeed failed in its application, and the latter only succeeded in the pretty experiment of elevating soap-bubbles by inflating them with hydrogen: he tried bladders, but the thinnest were too heavy; and tissue paper was permeable to the gas; it is singular he did not think of gold-beaters' skin, which, for similar purposes, had been recommended two centuries before, by SCALIGER the grammarian*.

The first ascent in a balloon filled with hydrogen, was made on the 1st of December, 1783, by Messrs. CHARLES and ROBERT, at Paris. In an hour and three-quarters, they alighted on the meadow of Nesle, twenty-five miles from the metropolis; and finding that the silk globe still retained great buoyant power, M. CHARLES ventured alone upon a second ascent. The sun had set, and the shades of evening were gradually condensing into the darkness of night; but his courage was rewarded by a most novel and sublime spectacle. He shot upwards with such celerity as to

* Supplement to *Encyclopædia Britannica*. Art. Aëronautics.

have attained the height of two miles in about ten minutes. The sun rose again to him in full orb, and from his lofty station he contemplated the fading luminary, and watched its parting beams till it once more sunk below the horizon. The vapors rising from the earth collected into clouds, and veiled it from his sight, while the pale rays of the moon scattered gleams of various hues over the fantastic and changing forms. The region in which the aëronaut now hovered was extremely cold; the balloon appeared fully distended, and upon opening the valve, the gas rushed out like a misty vapour into the external air. Prudence forbade this bold voyager to remain longer in such a situation; slowly therefore descending, he alighted in safety near the forest of Tour du Lay, having travelled about nine miles in thirty-five minutes. The barometer, at the greatest elevation, fell to 20·05 inches, and the thermometer sunk to 21° Fahrenheit; he therefore appears to have ascended to about 9,700 feet above the level of the sea.

The balloon has unfortunately proved but an abortive instrument in the hands of science. Messrs. BIOT and GAY-LUSSAC embarked from Paris on the 23rd of August, 1804, upon an aërial excursion devoted entirely to scientific inquiry. At the height of 13,000 feet, no peculiarity appeared to attach to electric or magnetic phenomena. On the 5th of the following September, GAY-LUSSAC undertook a second voyage alone, and attained the enormous height of 23,040 feet above the sea. Here he experienced excessive cold, his breathing was oppressed, and the pulse quickened; he, however, did not suffer the peril of his situation, or the peculiarities of his sensations, to distract his attention, and made several magnetic, electric, and hygrometric observations, without either novel or interesting results. Having alighted in safety in the neighbourhood of Rouen, he returned to Paris, and in the presence of M. THENARD, analyzed the air brought from the upper regions, which proved analogous in composition to that at the surface of the earth.

To return to CAVENDISH: having determined the specific gravity, and other abstract properties of hydrogen gas, he proceeded to examine the results of its combustion, and found that, when mixed in certain proportions with atmospheric air, it exploded on the contact of flame, and deposited moisture in the vessel used for the experiment, a circumstance first noticed by MACQUER in 1766, and distinctly referred by WATT to the production of water in 1783. The experimental proofs, however, were still insufficient, and were supplied by CAVENDISH, in a paper given to the Royal Society in 1784. He found that a stream of pure hydrogen, burned either in air or oxygen, produced a vapor condensible into pure water. The same product resulted from the rapid combustion of a mixture of inflammable and dephlogisticated airs (hydrogen and oxygen gases). These experiments were subsequently verified by analytical researches: water was decomposed by LAVOISIER, by passing steam through a red-hot tube containing iron, which absorbs its oxygen, and pure hydrogen is liberated in the gaseous form. The decomposing energies of electricity have also been applied to this fluid, and it is found uniformly to be resolved into one volume of oxygen and two of hydrogen, which disappear on passing an electric spark through the mixture, and are converted into their weight of pure water.

This discovery of the composition of water, jointly due to CAVENDISH and WATT, was a great step in chemical science, for it developed the hidden cause of many important phenomena of art and nature: no wonder, then, that the attention of theorists was especially fixed upon it, some applying it to the explication of all difficulties; others rejecting even legitimate conclusions, and unwilling to strike this favorite element from the list of simple bodies.

CAVENDISH was an enemy to the new Nomenclature of chemistry, and was fond of foretelling its downfall; he disliked all innovations that were not rendered absolutely necessary by the progress of experiment; and would never adopt new opinions, till fully and leisurely convinced of the fallacy of old ones.

While CAVENDISH was thus extending the boundaries of chemical science, SCHEELE* was diligently employed in similar pursuits, under the patronage and guidance of BERGMAN, of whom it has been emphatically said, "that his greatest discovery was the discovery of SCHEELE," for he was the first to remark his promising genius, and rising merit.

SCHEELE's publication, entitled *Chemical Observations and Experiments on Air and Fire*, is prefaced by an Introduction from the pen of his patron BERGMAN, setting forth the advantages of experimental science, and the benefits likely to result from the application of chemistry to the treatment and cure of diseases. Finding air necessary for the production of fire, SCHEELE first turned his attention to its analysis: he found that solution of liver of sulphur, and certain other sulphureous compounds, occasioned a diminution in the bulk of air to which they were exposed, equal to about one part in five; the flame of hydrogen, and that of sulphur, caused a similar decrease of bulk in air standing over water; and lime-water not being rendered in either case turbid by the residuum, no fixed air was formed. He then obtains *empyrean air*, (oxygen,) by the decomposition of nitric acid, and other processes; describes the method of transferring, collecting, and examining the gases; and endeavours to prove that *heat* is a compound of empyrean air and phlogiston; he also shows, by a direct experiment, that the absorption occasioned in atmospheric air by liver of sulphur, is referable to the abstraction of its empyrean portion; that it totally absorbs empyrean air; and that upon adding to the residuary portion of atmospheric air, a quantity of empyrean air equal to that absorbed by the sulphureous liquor, an air is again compounded, similar in all respects to that of the atmosphere. The identity of these investigations

* Scheele is among the fortunate few, who, starting from an obscure original, have attained the zenith of scientific eminence. He was born in 1742, at Stralsund, where his father was a tradesman. His youthful days were passed in the house of an apothecary at Gottenburgh, where, by singular perseverance, and that kind of industry which is prompted by strong natural inclination, he acquired a valuable stock of chemical information. In 1773, having removed to Upsal, accident brought him acquainted with Berg-

man, who became his friend and patron, and to whose honor be it told, that, when Scheele's reputation afterwards rose to such a height as threatened to eclipse his own, instead of listening to the voice of jealousy, which, on such occasions, is too common a frailty, he became more zealous in behalf of his rival, and more indefatigable in the service of his friend. Scheele afterwards removed to Köping, in the neighbourhood of Stockholm, where he died in 1786.

with those of PRIESTLEY, will not fail of being observed; but it must be recollected that they were entirely independent; and that although PRIESTLEY was in the field a little before him, SCHEELE was unacquainted with his proceedings.

The details concerning the nature of air, are followed by an inquiry into the properties of Heat and Light, which, though somewhat tainted by false theory, bears the stamp of an able and original mind. Adverting to the reflection of the rays from a common fire, by a concave metallic mirror, he remarks, that they passed in straight lines, without suffering any derangement from currents or undulations in the atmosphere which they traverse; that glass intercepts the heat, but not the light; that a mirror of glass reflects the light, but absorbs the heat, whereas metal reflects both: the metal, therefore, if clean, does not become heated; but, if blackened over a smoking candle, it then absorbs heat, and becomes very warm. He notices the distinction between heated air, and heat emanating in straight lines: "represent to yourself a little hillock of burning coals; in this case, the heat darting from this hillock all around, is that which may be reflected by a metallic polished plate; that, on the contrary, which rises upwards, and may be driven by winds to and fro, unites with air. I call the first kind, by way of distinction, *radiant heat*." Discussing the phenomena of solar and terrestrial radiation, he considers their apparent differences to result, not from any absolute difference in the nature of the emanating particles, but in their quantity. "There is no doubt," he says, "about the light of the sun and that of a burning candle being the same thing; for this affects the eye in the same manner as the sun, and represents the same colors through the prism; but being weaker, it is no wonder that its beams, collected in a burning-glass, will not burn: nor is there any doubt about light being a body, in the same manner as heat; but I cannot persuade myself that light and heat are the same thing, since experiment proves the contrary." Finding that light blackened nitrate of silver, though heat alone had no effect upon it, he considers light as containing an inflammable principle; and shows that *luna cornea*, after long exposure to the sun's rays, is no longer perfectly soluble in ammonia, but leaves a portion of reduced silver; he also shows, that when put into water, it forms muriatic acid in the light, but not in the dark; and that the violet rays produce these effects more rapidly and powerfully than the other colored rays, and even than white light.

Among these Experiments on Air and Fire, some curious facts are detailed, respecting the spontaneously inflammable compound discovered early in the last century by HOMBERG, and called *Pyrophorus*; it is shown that potash is necessary to its formation, and that alum crystallized by ammonia, is unfit for its production. The evolution of hydrogen, during the action of iron upon sulphur, and of nitrogen in the detonation of fulminating gold, are also among the facts contained in this essay; as well as a variety of curious circumstances relating to the effect of vegetation and respiration upon air; and it closes with an account of the properties of Sulphuretted Hydrogen.

Exclusive of the experimental details, there is little to praise in the *Treatise on Air and Fire*, for the theories which it contains are often

strained and illicit, and do not easily admit of being rendered intelligible by the translation of the phlogistic language into that of the modern school: nor are SCHEELE's detached essays altogether free from similar blemishes; but then they are so rich in facts, that we the more easily overlook theoretical failings. His dissertation on Manganese, for instance, with a description of the principal salts of that metal, contains the important discovery of Dephlogisticated Muriatic Acid, or, as it is now termed, Chlorine; and his views respecting it, and the nature of the muriatic acid, are remarkably correct, and perfectly intelligible in present theory, if we substitute hydrogen for phlogiston; it will then be found, that muriatic acid is regenerated by the addition of hydrogen to chlorine; and that hydrogen is evolved by the abstraction of chlorine from muriatic acid.

BERTHOLLET's hypothesis of the nature of chlorine for a time superseded the theory of SCHEELE, and under the name of Oxymuriatic Acid, it was regarded as a compound of oxygen and muriatic acid; but, in 1811, Sir H. Davy, in an important dissertation on the subject, published in the *Philosophical Transactions*, demonstrated the errors of the French school, revived the doctrine of SCHEELE, and established it by a body of evidence now generally received. Berthollet, however, has the distinguished merit of first suggesting the application of chlorine to bleaching upon the large scale.

In his essays on Fluor Spar, and its acid, SCHEELE has committed several errors, among which the most glaring is the conclusion which he draws respecting the formation of silicious earth. When powdered fluor spar is distilled with sulphuric acid in a glass retort, the silica of the glass is dissolved by the acid of the fluor, carried over with it in the gaseous state, and in part deposited in the receiver containing water; SCHEELE inferred that silicious earth was here *formed* by the union of fluoric acid and water; and persisting in his error, he endeavours to show that the same formation ensues in metallic vessels, and therefore independent of glass; but he takes no due precautions against the presence of silica in the fluor spar which he used. Yet there is much to praise in the methods of analysis employed in investigating the nature of this singular body; it is a subject full of difficulties, and can scarcely be called complete even at the present day, though it has engaged the attention of the most acute analysts. The acids of arsenic, and of molybdenum, were first examined by SCHEELE; and he first showed the difference between Molybdenum and Plumbago, and pointed out the existence of carbon in the latter.

In 1778, SCHEELE made known the preparation of Arsenite of Copper, and recommended it as an useful and permanent color in oil and water painting; and, in 1779, he took up the important subject of the decomposition of neutral salts by unslaked lime and iron. He found upon the iron hoops of a tub of salted turnips, which had been placed in a damp cellar, a quantity of salt resembling mineral alkali, and was struck with the circumstance, "knowing that the attraction of acid of salt is weaker for iron than for mineral alkali." He dipped plates of several other metals into solutions of common, and Glauber's salt, but found that iron only was effectual in their decomposition, and that the action was more rapid in a damp cellar, than elsewhere; he also found that quicklime

decomposed those salts in the same situation; and that the decomposition was partly dependent upon the presence of carbonic acid in the atmosphere of the vault.

In his essays on Milk, and Sugar-of-milk, there are many curious circumstances respecting the action of re-agents upon that liquid; and these papers deserve particular notice, as among the earliest specimens of the analysis of animal fluids. SCHEELE observes that, from his experiments, it appears "that the acid of milk is an acid of a peculiar kind; and though it expels the vinegar from acetated vegetable alkali, yet it seems destined, if I may so speak, to be vinegar." He attributes the difference, to the want of some ferment; and shows that the addition of a little brandy to milk, causes it, when fermented, to afford good vinegar. The method of obtaining the Citric and some other vegetable acids, by decomposing their compounds with lime, by sulphuric acid, is also among SCHEELE'S discoveries; and his essays on Tungsten, on the preparation of Calomel in the humid way, on Urinary Calculi, on Ether, and on Benzoic acid, each contain important facts, and display new modes of inquiry: they deserve the perusal of those who may be engaged in investigations relating to the several subjects of which they treat.

The last essay to which I shall advert in this sketch of SCHEELE'S discoveries, was published in 1782, and is entitled *Experiments on the Coloring Matter of Prussian Blue*. This very singular substance was accidentally discovered early in the last century, by DIESBACH, a color-maker at Berlin: the preparation was, however, kept secret, till published by WOODWARD, in 1724. In 1752, MACQUER'S dissertation upon it presented a connected view of its chemical history, which, however, was imperfect and unsatisfactory. SCHEELE directed his attention to the discovery of the principle upon which its color depended. He shows, that the salt produced by digesting Prussian blue in caustic potash, is a triple compound of the coloring principle, iron, and potash; iron being, as he supposes, the medium by which the coloring principle is attached to the alkali: this salt he decomposed, by distilling its aqueous solution with a small quantity of concentrated vitriolic acid, and the liquor which passed into the receiver carried with it a great portion of the coloring principle, which has since been termed *Prussic Acid*. SCHEELE then goes on to show that the action of this acid, in its pure state, upon metallic solutions, is very different from that which it exhibits when combined with alkalis. United with lime, he found that it afforded precipitates in the greater number of metallic solutions. Our author enters into much interesting speculation and experiment, relating to the nature of this coloring principle; and considering the difficulty of the subject, treats it with perspicuity and success. This dissertation on Prussian blue, was nearly his last contribution to the science which he had so much embellished and improved, for he died in 1786, at the age of forty-four.

It requires no deep inquiry, or minute investigation, to detect, in the researches of PRIESTLEY, SCHEELE, and CAVENDISH, the materials of which their contemporary, LAVOISIER, aided by several celebrated chemists of the French school, constructed his new theory; and a retrospect of the works of MAYOW and HOOKE will show, that the Antiphlogistic System almost necessarily arose, out of a combination of their views with the more

modern discoveries. In maintaining, however, that the materials employed in raising this celebrated system were of foreign, and chiefly of British origin, we must not be understood as detracting from the indisputable merit of those, to whose persevering diligence Chemistry owes so much of its present importance; by whom the scattered and unconnected facts of the science were brought together and arranged; and who cleared its paths of the numerous obstructions with which they were previously beset.

§ XIII.

THE numerous and important contributions with which the eminent but unfortunate LAVOISIER* enriched the chemistry of his time, are to be found in the *Memoirs of the Royal Academy of Sciences of Paris*; but as he has chiefly been celebrated as a theorist, I shall here confine myself to such of his inquiries as bear upon that memorable reform in the science, by which a new nomenclature was introduced, and which ended in the banishment of phlogiston. In this reform, LAVOISIER took the lead; and though his original investigations connected with it are few and comparatively unimportant, he availed himself with so much skill, and success, of the labors of others, as, by placing them in new points of view, and exhibiting their unexpected applications, to render them almost his own. LAVOISIER's character has, in some measure, suffered by the misguided zeal of his admiring commentators, who, not satisfied with allowing him due merit for the logical precision, and sagacity of induction, which he brought into chemistry, have represented him as having the experimental activity of PRIESTLEY, and the laborious diligence of SCHEELE. But LAVOISIER, though a great architect in the science, labored little in the quarry; his materials were chiefly shaped to his hand, and his skill was displayed in their arrangement and combination.

A connected view of his principal reasonings and most prominent researches, will be found in his *Elémens de Chimie*, published in Paris, in 1789. This work, in every way important, is divided into three principal sections: the first treats of the formation and decomposition of aëriform fluids, of the combustion of simple bodies, and the formation of acids: the second, of the combination of acids with salifiable bases, and of the formation of neutral salts: and the third, of the instruments and operations of chemistry.

The first section opens with a discussion concerning the Nature and Operations of Heat, which he defines as a real and material substance, or a very subtile fluid, separating the particles of bodies from each other, by insinuating itself among them. This exquisitely attenuated substance, he calls *Caloric*; and though he allows that light, in many instances, produces phenomena analogous to those of heat, though they have certain qualities in common, their identity not having been demonstrated, they are to be considered as distinct; he then dwells upon the requisite caution in investigating the properties of caloric, since they are known

* Born in 1743 at Paris, where he fell a victim to the Revolution, on the 8th of May, 1794.

only by fleeting and difficultly ascertainable effects: "It is in those things," he says, "which we neither see nor feel, that it is especially necessary to guard against the extravagances of the imagination, which, always inclining to overstep the bounds of truth, is difficultly restrained by the narrow limits of facts." The influence of heat upon the states of bodies is then illustrated, and their relative capacities for heat alluded to. He says that solidity, liquidity, and aëriform elasticity, are only three different states of existence of the same matter, or three particular modifications which almost all substances are susceptible of assuming successively, and which solely depend upon the degree of temperature to which they are exposed, or, in other words, "upon the quantity of caloric with which they are penetrated." In consequence of this influence of caloric, the possible existence of certain metallic substances in our atmosphere is inferred; "such a substance, for instance, a little more volatile than mercury, might exist there." LAVOISIER then proceeds to the analysis of atmospheric air, which he effects by exposing fifty cubical inches of it to heated mercury; it undergoes a decrease equal to one-sixth of its original bulk, and becomes unfit for respiration and combustion; at the same time, the quicksilver is partly converted into a reddish matter, 45 grains of which heated red-hot in a proper retort, afforded 41.5 of running mercury, and 7 or 8 cubical inches of gas, eminently supporting combustion, and being the dephlogisticated air discovered by PRIESTLEY. The mixture of the 42 cubical inches of the mephitic air of the retort, with the 8 cubical inches of dephlogisticated air, separated from the mercury, reproduce 50 cubic inches of atmospheric air.

LAVOISIER considered all aëriform fluids as compounds of a ponderable basis, with caloric and light: in the above experiment, the ponderable part of the dephlogisticated air unites to the quicksilver, but the union is effected so slowly, that the phenomena of combustion are not perceived; if, however, red-hot iron wire be introduced into the air evolved from the red compound of quicksilver, it acts readily upon it, and its decomposition is attended by the copious evolution of heat and light, while the iron undergoes an increase in weight equivalent to that of the air absorbed.

In discussing the principles of nomenclature, most applicable to the different aëriform fluids, LAVOISIER retains, after the example of MACQUER, the word *gas*, used first by VAN HELMONT, as a generic term for all that differ from atmospheric air: he shows, that one of the most general properties of vital or dephlogisticated air, is, to form *acids*, and hence he gives it the name of *oxygen gas*; the other element of the atmosphere is called *azotic gas*, from its fatal effects upon animal life, a term, "commendable," says LAVOISIER, "because it only expresses a matter of fact."

The combustion of sulphur, phosphorus, and carbon, is next shown to be attended with the same phenomena as that of iron, namely, the extrication of heat and light, and the union of the ponderable part of the oxygen with the combustible; and the principles of nomenclature applicable to these different compounds are developed. Where oxygen does *not* form an acid, its compounds are termed *oxides*; and where more than one oxide, or acid, is formed, the termination of the base

indicates its nature: thus there are four compounds of nitrogen with oxygen, two oxides, and two acids; the former are respectively termed *nitrous* and *nitric oxides*; and the latter, *nitrous* and *nitric acids*; the *minimum* and *maximum* of oxygen being in each case designated by the termination *ous* and *ic*. The term *hydrogen* is applied to inflammable air, shown by CAVENDISH to be the basis of *water*; and fixed air is called *carbonic acid*, since it is identical with the result of the combustion of charcoal, or carbon, in oxygen. In connection with the latter subject, LAVOISIER made the important discovery of the production of carbonic acid by the combustion of the diamond. The destruction of this gem by fire, was demonstrated by the Florentine Academicians as early as 1690; they exposed a diamond to the focus of a burning lens, and found that it entirely evaporated; and Francis the First, of Germany, witnessed the same phenomenon in the heat of a furnace. LAVOISIER proved that the diamond underwent no change when air was excluded; and that, when ignited in oxygen gas, it produced carbonic acid: whence the inevitable conclusion, that the diamond and charcoal are identical in their nature; and that the vast difference in their appearance, and mechanical qualities, is the result of aggregation; that the one is crystallized; the other in a less indurated form. Unprecedented as such an idea may seem, it is not only warranted by the experiments of LAVOISIER and others, but also in some degree supported by analogy. Thus, when argillaceous earth, which is a white pulverulent substance, is aggregated by mechanical attraction into a crystalline form, it constitutes the sapphire, one of the hardest and least destructible of the gems. In one state, the earth is soft, and readily soluble in acids; in the other, its insolubility equals its induration: but there is one anomaly, relating to the conducting power of the diamond and charcoal in regard to electricity; the former ranks among the non-conductors, the latter is a good conductor; and hitherto mechanical texture has not been clearly shown, in any strictly analogous cases, to interfere with the power of conducting electricity.

Among those who have further explored the phenomena of the combustion of the diamond, and who have verified and extended the original views of LAVOISIER, we find the names of some of the most eminent European Philosophers. Few subjects in Chemistry have been so carefully pursued, and the united results of different experimentalists have rarely tallied with the precision with which these researches present*.

* That the quantity of carbonic acid, afforded by a given weight of diamond, is the same as that yielded by a similar quantity of charcoal, is the great proof of the identity of those apparently dissimilar substances; this was demonstrated in the year 1796, by the refined and elegant experiments of the late Mr. Tennant.

Mr. Smithson Tennant was a profound philosopher, and a matchless companion: "his learning was without pedantry; his wit without sarcasm;—he was deep, but always clear; gentle, but never dull." To those who knew him not, it is scarcely possible to offer an adequate representation of his singularly pleasing and

enlightened character; by those who enjoyed his acquaintance, and partook of his social hours, his extent of knowledge, his happy and unrivalled talent for conversation, his harmless but brilliant flashes of merriment, and all his amiable peculiarities, can never be forgotten. Mr. Tennant was born in Yorkshire in 1761, and died at Boulogne in 1815. He was the discoverer of the metals Iridium and Osmium, and the author of several important contributions to chemical science.

See Biographical Account of Smithson Tennant, Esq., in THOMSON'S *Annals of Philosophy*, vol. vi.

LAVOISIER was the first who examined with requisite accuracy the products of the distillation of vegetable and animal substances, and who drew a proper line of distinction between the *educts* and *products* thus afforded; he also inquired, with more success than any of his predecessors, into the phenomena of *fermentation*, and by examining the contents of certain vegetable juices previous to and after that process, he drew some very curious conclusions respecting the changes that take place.

In his observations upon *salifiable bases*, and the formation of *neutral salts*, LAVOISIER has described the phenomena of the solution of metals in the various acids: he adverts to the oxidizement of the metals previous to their solution, and to the consequent liberation of hydrogen; and has the following acute surmise respecting the nature of the alkaline earths, which then were considered as elementary bodies:—"From these phenomena it appears that oxygen is the bond of union between metals and acids, and from this we are led to suppose that oxygen is contained in all substances which have a strong affinity with acids; hence it is very probable that the four eminently salifiable earths contain oxygen, and that their capability of uniting with acids is produced by the intermediation of that element. What I have formerly noticed relative to these earths, namely, that they may very possibly be metallic oxides, with which oxygen has a stronger affinity than with carbon, and consequently are not reducible by any known means, is considerably strengthened by the above considerations." Sir H. DAVY, in showing the combustibility of the metals of the alkalis in carbonic acid, has verified this anticipation.

In the second part of the *Elements*, LAVOISIER treats of the formation of Neutral Salts, and throws out new and important views relating to the constitution of chemical compounds. Speaking of the influence of Light as a chemical agent, he adverts to its singular action upon the vegetable kingdom, and supposes that it combines with certain parts of vegetables, and that the green of their leaves, and the various colors of their flowers, are chiefly owing to this combination. "This much," he says, "is certain, that plants which grow in darkness are perfectly white, languid, and unhealthy, and that to make them acquire vigor, and recover their natural colors, the direct influence of light is absolutely necessary. Somewhat similar takes place even in animals. Mankind degenerate to a certain degree when employed in sedentary manufactures, or living in crowded houses, or in the narrow lanes of large cities; whereas they improve in their nature and constitution in most of the country labors which are carried on in the open air."

LAVOISIER incorrectly refers the influence of light to its direct combination; but it rather appears to modify, or exalt, the mutual agencies of bodies: of this we have some remarkable instances; as in the action of chlorine upon hydrogen and upon carbonic oxide; and of chlorine and several of the chlorides, upon water; from which it occasions the evolution of oxygen, and the production of muriatic acid; this change gave rise to the idea of the existence of oxygen and muriatic acid as the components of chlorine; the agency of water and the nature of muriatic acid not having been taken into account.

In his observations on the combinations of oxygen, the conditions requisite to the oxidizement of bodies are mentioned; such as the dimi-

nution of aggregation by heat, which causes many substances to attract the oxygen of the atmosphere; their ignition with nitre, or with chlorate of potassa; and their solution in certain acids, especially the nitric. The combinations of the different combustible substances are next reviewed, and those of the acids and some other compound bodies.

The third part of the *Elements* is occupied with the description of a variety of chemical operations, which were exceedingly improved and extended by LAVOISIER. He shines as the inventor of costly and complicated apparatus, the greater part of which might, however, have been superseded by simpler and cheaper utensils.

This sketch of the contents of LAVOISIER'S *Elements of Chemistry* will sufficiently show the extent and perspicuity of his views as a theorist; and though the arrangement is open to objection, it was calculated for the use of the student, and fitted to display the strongest parts of the anti-phlogistic system in the most favorable light: it was, indeed, impossible that any one of unbiassed judgment, could seriously retain the phlogistic doctrines, after the perusal of this masterly refutation. But if we look for the abstract facts upon which this refutation rests, we shall search in vain, either in the works of LAVOISIER, or in those of his contemporaries: they were furnished from other quarters, and will, I think, chiefly be found in the writings of MAYOW and HOOKE, and in those of PRIESTLEY and SCHEELE. The prominent features of the French theory are its explanation of the phenomena of combustion and of acidification, the presence of oxygen being deemed essential in both cases. That air is the food of fire was known in the remotest ages; that it causes the increase of weight sustained by metals during their fusion and calcination, was shown by REY early in the seventeenth century; that a part only of the atmosphere, is concerned in the support of flame, was explained by HOOKE in 1667; and that the vital or igneous spirit, as he terms it, of the atmosphere, is concerned in the formation of acids, was asserted by MAYOW in 1674. Here, without advancing into the eighteenth century, we have, in explicit detail, all the facts and arguments requisite for the construction of the French theory; but if to these we add the discovery of Oxygen by PRIESTLEY, and of the composition of water by CAVENDISH and WATT, what then becomes of its claim to originality?

It must be regretted that those who have censured LAVOISIER with occasional uncandid and unacknowledged appropriation of the thoughts of others, have some grounds for the accusation. In bringing forward his theory of combustion, why did he not refer to the opinions of REY and MAYOW? why refuse praise and acknowledgment to BLACK, and SCHEELE, and CAVENDISH; or why appropriate the discovery of oxygen, in the face of the prior, indisputable, and known claims, of his friend and contemporary, PRIESTLEY? These are questions we cannot now answer; but those who have grounded indiscriminate and severe censure upon such accusations, have neither been animated by the unprejudiced spirit of true philosophy, nor guided by the unbiassed love of truth. It must be remembered that LAVOISIER was never fairly confronted by these rivals and antagonists; that unintentional inadvertency sometimes accompanies scientific ardor; that, in the eagerness of pursuit, he may have neglected that which, in a calmer hour, he would have seen, regretted, and acknowledged;

and that, in the hurry of discussion and heat of controversy, he was suddenly summoned to eternity*.

* Two scarce volumes of the posthumous works of Lavoisier are extant, consisting, in great measure, of extracts from, and sketches of, his different papers read before the Royal Academy of Sciences; but several original Observations and Essays are also dispersed among them. They, in some degree, justify the observations which I have made in the text, that, had Lavoisier lived, he would have done more justice to his predecessors and contemporaries, for he candidly reviews their opinions, and compares them with his own; at the same time, the following passage cannot be regarded as perfectly candid towards Rey, who, as I have shown above, founded his arguments, not upon hypothesis, but upon experiment.

I insert a long quotation, that there may be no misunderstanding upon the subject.

After stating the prevailing phlogistic notions entertained at that period, he proceeds as follows:—"Tel étoit l'état des connoissances, lorsqu'une suite d'expériences, entreprises en 1772 sur les différentes espèces d'air, ou de gaz qui se dégagent dans les effervescences et dans un grand nombre d'opérations chimiques, me firent connoître, d'une manière démonstrative, quelle étoit la cause de l'augmentation de poids qu'acquîèrent les métaux lorsqu'on les expose à l'action du feu. J'ignorois alors ce que Jean Rey avoit écrit à ce sujet en 1630; et quand je l'aurois connu, je n'aurois pu regarder son opinion à cet égard, que comme une assertion vague, propre à faire honneur au génie de l'auteur, mais qui ne dispensait pas les chimistes de constater la vérité de son opinion par des expériences. J'étois jeune, j'étois nouvellement entré dans la carrière des sciences, j'étois avide de gloire, et je crus devoir prendre quelques précautions pour m'assurer la propriété de ma découverte. Il y avoit à cette époque, une correspondance habituelle entre les savans de France et ceux d'Angleterre; il régnoit entre les deux nations, une sorte de rivalité qui donnoit de l'importance aux expériences nouvelles, et qui portoit quelquefois les écrivains de l'une ou de l'autre nation, à les contester à leur véritable auteur; je crus donc devoir déposer, le 1^{er} Novembre, 1772, l'écrit suivant cacheté,

entre les mains du Secrétaire de l'Académie. Ce dépôt a été ouvert à la séance du 5^{me} Mai suivant, et mention du tout a été faite en tête de l'écrit. Il étoit conçu en ces termes:—

"Il y a environ huit jours que j'ai découvert, que le soufre en brûlant, loin de perdre de son poids, en acquiéroit au contraire; c'est à dire, que d'une livre de soufre on pouvoit retirer beaucoup plus d'une livre d'acide vitriolique, abstraction faite de l'humidité de l'air; il en est de même du phosphore; cette augmentation de poids vient d'une quantité prodigieuse d'air qui se fixe pendant la combustion, et qui se combine avec les vapeurs.

"Cette découverte que j'ai constatée par des expériences que je regarde comme décisives, m'a fait penser que ce qui s'observoit dans la combustion du soufre et du phosphore, pouvoit bien avoir lieu à l'égard de tous les corps qui acquièrent du poids par la combustion et la calcination: et je me suis persuadé, que l'augmentation de poids des *chaux* métalliques, tenoit à la même cause. L'expérience a complètement confirmé mes conjectures: j'ai fait la réduction de la litharge dans des vaisseaux fermés, avec l'appareil de Hales, et j'ai observé qu'il se dégageoit, au moment du passage de la *chaux* en métal, une quantité considérable d'air, et que cet air formoit un volume au moins mille fois plus grand que la quantité de litharge employée. Cette découverte me paroissant une des plus intéressantes qui ait été faite depuis Stahl, j'ai cru devoir m'en assurer la propriété, en faisant le présent dépôt entre les mains du Secrétaire de l'Académie, pour demeurer secret jusqu'au moment où je publierais mes expériences.

(Signé) "LAVOISIER."

"En rapprochant cette première notice de celle que j'avois déposée à l'Académie le 20^{me} Octobre précédent, sur la combustion du phosphore, du mémoire que j'ai lu à l'Académie à sa séance publique de Pâques 1773, enfin, de ceux que j'ai successivement publiés, il est aisé de voir que j'avois conçu dès 1772, tout l'ensemble du système que j'ai publié depuis sur la combustion. Cette théorie à laquelle j'ai donné de nombreux développemens en 1777, et que j'ai [porté,

Although LAVOISIER made few original discoveries, his talents were perhaps more usefully employed in setting forth and elucidating the researches of others, a task which he performed with great skill and success: in reviewing hypotheses, he diligently contrasts them with facts; weight and measure, which had been introduced into chemistry by BERGMAN, were strictly insisted upon in all his manipulations; and in his hands chemistry assumed the features of a new branch of knowledge, and put on its present character.

Connected with the labors of LAVOISIER is the celebrated reform of *chemical nomenclature* effected by him and his associates, among the most eminent of whom we may enumerate GUYTON MORVEAU*, FOURCROY†, and CHAPTAL‡. The former, amidst varied occupations, pursued

presque dès cette époque à l'état où elle est aujourd'hui, n'a commencé à être enseignée par Fourcroy, que dans l'hiver de 1786 à 1787; elle n'a été adoptée par Guyton Morveau, qu'à une époque postérieure: enfin, en 1785 Berthollet écrivait encore dans le système du phlogistique. *Cette théorie n'est donc pas, comme je l'entends dire, la théorie des Chimistes François: elle est la mienne; et c'est une propriété que je réclame auprès de mes contemporains et de la postérité.*"

* Born at Dijon, 1737; died 1815. "Guyton Morveau," says Davy, "was very old when I made his acquaintance; between seventy and eighty, and very feeble. Though he had been a violent republican, he was Bonaparte's director of the mint, and a baron of the empire. His manners were mild and conciliatory; and it is a proof of the energy of his mind, that having promised his vote to a person, as Corresponding Member of the Institute, he kept his promise, and my election wanted only his voice to be unanimous. Having never, when in France, inquired into the intrigues connected with elections, or interested myself about them, I should not have known this, had he not himself told me so when I dined afterwards at his house." —*Davy's Life*, by Dr. JOHN DAVY.

† Born at Paris, 1755; died, 1809.

‡ I have extracted the following notice of Chaptal from the address of H. R. H. the Duke of Sussex, delivered at the Anniversary Meeting of the Royal Society, November 30, 1832:—

"Jean Antoine Chaptal, Comte de Chanteloup, was born in 1756, and died in April last, in the 76th year of his age. He was Professor of Chemistry at Montpellier, before the Revolution, and was one of the most active cultivators of chemical science before that event, in conjunction

with Monge, Fourcroy, Berthollet, Guyton de Morveau, and the illustrious Lavoisier. In the year 1793, upon the threatened invasion of France by the Allies, when saltpetre was not to be procured in sufficient quantities for the manufacture of the powder wanted by the French armies, he was invited by the Committee of Public Safety to superintend the establishments for that purpose; and his chemical knowledge so greatly improved the method followed in its manufacture, as in a very short time to make the produce greatly exceed the demand. He was made *Ministre de l'Intérieur* by Napoleon, and continued under the Empire to fill many important situations. He was the author of considerable works on chemistry, on the application of chemistry to the arts, on the application of chemistry to agriculture, on the art of making wines, and on the art of dyeing cotton and wool, which are written in a very perspicuous and elegant style, and which have enjoyed a very considerable popularity in France. The labours of his whole life, in fact, were devoted to the improvement of those manufactures whose perfection depended more or less upon the most correct and economical application of chemical principles; and, after his distinguished countryman, Berthollet, he must be placed in the first rank of those who have benefited the arts through the medium of chemical science."

"Chaptal," says Sir H. Davy, "for a long while Bonaparte's Minister of the Interior, was an active, amusing, intriguing courtier and chemist, and somewhat acquainted with the state of the chemical arts in France. Not very exact in conversation, and a little boasting, yet good natured, and with lively man-

chemistry with successful diligence, and, had he given nothing else to the science, his name deserves to be transmitted to posterity as the inventor of the means of destroying infection by acid vapors, the efficacy of which he first pointed out in the year 1773. His first essay on the reform of nomenclature was published in the *Journal de Physique* for May, 1782, and although it was strenuously opposed by the colossal power of the Royal Academy of Paris, the plan was not only afterwards approved, but prosecuted by the eminent chemists of that metropolis. The different papers and correspondence relating to this subject are, in many respects, curious and interesting, from the difference of opinion which prevailed respecting the terms he adopted, and the ultimate benefit likely to result from the reformation. FOURCROY is a well-known name in the chemical world: his works rank among the most celebrated which France has produced in the science: he is the first author who published a *System* of chemistry. CHAPTAL was a successful contributor to the Chemistry of the Arts.

The difficulties attending an entire reform in the nomenclature of chemical science may be well imagined; they were encountered with considerable address; and it must be confessed that, while it particularly tended to the dissemination of the anti-phlogistic doctrines, it facilitated the general acquisition of the science; the ludicrous terms of the alchemists were rejected, and names founded upon the nature of compound bodies, and upon the leading qualities of elementary substances, became their more sensible substitutes. It is true, that the progress of science has rendered much of the French nomenclature objectionable, and that it has been requisite to modify many of its terms, more especially such as were founded on erroneous theory: others, though objectionable, have been retained, rather than submit to the serious inconvenience to which repeated innovations tend; and nothing short of absolute necessity can justify us in changing old and accepted terms, for those of more recent coinage. In the selection of names necessarily new, some leading and obvious property, independent of theory, should be selected as their basis; such terms as *iodine*, *bromine*, and *chlorine*, are in this respect unexceptionable. To the subjoined opinion upon this subject, by Sir H. DAVY*, I entirely subscribe:—

“Simplicity and precision ought to be the characteristics of a scientific nomenclature; words should signify things, or the analogies of things, and not opinions. If all the elements were certainly known, the principle adopted by LAVOISIER would have possessed an admirable application; but a substance in one age supposed to be simple, in another is proved to be compound; and *vice versâ*. A theoretical nomenclature is liable to continued alteration; *oxygenated muriatic acid* is as improper a name as *dephlogisticated marine acid*. Every school believes itself in the right; and if every school assumes to itself the liberty of altering the names of chemical substances, in consequence of new ideas of their composition or

ners, and quiet and ready conversation. More a man of the world than any of the savants of his day in France. It is said that he was author of Napoleon's decrees aimed at the commerce of England; if

so, he has contributed more than any other individual, except his master, to the military glory of the modern Briton.”

* *Elements of Chemical Philosophy*, pp. 46, 47.

decomposition, there can be no permanency in the language of the science; it must always be confused and uncertain. Bodies, which are similar to each other, should always be classed together; and there is a presumption that their composition is analogous. Metals, earths, alkalies, are appropriate names for the bodies they represent, and independent of all speculative views; whereas, oxides, sulphurets, and muriates, are terms founded upon opinions of the composition of bodies, some of which have been already found erroneous. The least dangerous mode of giving a systematic form to a language seems to be to signify the analogies of substances by some common sign affixed to the beginning, or the termination, of the word. Thus, as the metals have been distinguished by a termination in *um*, as *aurum*, so their calciform, or oxidated state, might have been denoted by a termination in *a*, as *aura*; and no progress, however great, in the science, could render it necessary that such a mode of appellation should be changed. Moreover, the principle of a composite nomenclature must always be very limited. It is scarcely possible to represent bodies consisting of five or six elements in this way, and yet it is in such difficult cases that a name implying a chemical truth would be most useful."

Among the causes that have contributed to the recent progress of chemical science, we have already had occasion to advert to the *doctrine of definite proportionals*, which has enabled us to submit many of the phenomena of chemistry to calculation, and which promises to elucidate some of its most abstruse parts upon mathematical principles; but the chief source of the rapid advancement of chemistry during the present age, is doubtless the discovery of *the relation of electrical to chemical changes*; a discovery which has unfolded entirely new views of the mutual agencies of bodies, and which has equally furnished the theoretical and practical chemist with materials for speculative and experimental inquiry.

The curious experiments of GALVANI upon the convulsions excited in the limbs of animals, by the application of certain metals to their muscular and nervous fibres, led VOLTA to investigate the cause of such phenomena, and to attempt the accumulation of the electricity, to which he suspected they were to be referred: this he attained by successive alternations of different metals with substances acting chemically upon one of them; and he found that the extremities of such a pile were in opposite electrical states, and that the intensity of the electricity augmented with the number of alternations. This instrument has been productive of vast discoveries, which are yet far from exhausted, and has given rise, in the hands of DAVY, to a new and curious department of chemical philosophy, into the history of which I shall enter a little more in detail, chiefly with a view of showing the singular talent and sagacity with which a difficult and intricate branch of science was successfully pursued and illustrated by that eminent individual.

It appears, from the "*additional observations*," appended to his *Chemical Researches, upon Nitrous Oxide, &c.*, published in 1800, that Sir H. DAVY had no sooner heard of VOLTA's researches, than his mind was awakened to their bearings upon chemical changes; and from that period, to the time of his first publication upon the subject, he seems not to have lost sight of the inquiry; indeed it was his characteristic habit

to examine without delay all novel results of other philosophers, and when he had confirmed their accuracy, he generally rendered them subservient to further discovery. Accordingly, we find that the first paper which he presented to the Royal Society (read the 18th of June, 1801), was "*An Account of some Galvanic Combinations formed by the Arrangement of single metallic Plates and Fluids, analogous to the Galvanic Apparatus of Volta,*" and it contains several curious and interesting facts upon a subject which now began to excite general attention, and attracted the notice of many skilful experimentalists. The first harvest of fame, however, in this field of inquiry, was reserved for DAVY; and the *Bakerian Lecture* for 1806 contains a series of propositions and experiments, in reference to the chemical agencies of electricity, which at once display the masterly energies of the author's mind in passing from experiment to theory, and in the employment of that theory as the source of new, profound, and elaborate researches. About the time this paper was published, a great and important question respecting the agencies of electricity was undecided; it was not known whether electricity had the power of *generating* certain forms of matter, or whether they were merely *elicited*, by its influence, from compounds which escaped common modes of detection. Water, for instance, was found not merely to be resolved into its ultimate gaseous components, but their evolution was constantly connected with the appearance of acid and alkaline matter, and *that*, although every precaution was apparently taken to exclude foreign matters and all sources of impurity. Hence it was imagined that water either contained the elements of these bodies, or that it produced them by uniting with the electric fluids, or that they were actually conveyed, by some mysterious route, from the cells of the pile; indeed, it would be useless to enumerate all the speculations originating in these paradoxical phenomena; but it will be profitable to glance at the manner in which the difficulties were encountered by our author. He first repeated all that had been done by others, and criticized and compared their proceedings; he then electrized distilled water, and found, as they had found, the evolution of saline, alkaline, and acid bodies; but he also found that the more rigidly he purified the water, the smaller was the evolution of these products; a fact militating against their supposed source; still, however, they made their appearance. He now directed his attention to the vessels which were used, and succeeded in referring to *them* several extraneous bodies; thus glass, porcelain, and several mineral substances, yielded more or less foreign matter, which was successfully excluded when gold or platinum was substituted; but still, water which had been redistilled at a low temperature in a silver alembic, did afford acid and alkali; the source of this was next traced to the hands of the operator, and the accidental contact of test-papers, all which were consequently avoided, with a proportionate diminution of the problematical appearances; but they were yet present, for notwithstanding all precautions, litmus was reddened in the positive, and turmeric rendered brown in the negative vessel: it was now, however, found that the acid and alkali were nitric acid and ammonia; substances producible by new arrangements of the elements of air and water; and accordingly when very pure water, carefully deprived, and kept from the contact, of air, was electrized *in vacuo*,

in cones of gold, which had not been *handled*, nothing but oxygen and hydrogen were elicited from it.

The question, therefore, concerning the origin of the appearances cited, was now so far satisfactorily determined. He then entered into many valuable contingent inquiries, and proves this essential fact, that electricity has the power not merely of rendering evident the smallest traces of foreign matter, but of decomposing compounds with apparent facility and perfection, the elements of which are held together by the strongest chemical attractive force; whence it was concluded that substances, hitherto deemed simple or elementary, might, under this all-powerful decomposing agent, afford evidence of a compound nature, and yield either known or new elementary bodies. The inquiry was accordingly resumed under this new light; and the Bakerian Lecture, read to the Royal Society, in November, 1807, contains the results to which it led. The first substances which occurred as likely to afford successful and novel information were the fixed alkalis. Upon subjecting caustic potassa to the action of the voltaic pile, it was found not to conduct electricity; and when its aqueous solution was used, the water only appeared to suffer decomposition. After several unsuccessful trials, it was at length found that the alkali, gently breathed upon, became sufficiently moist to suffer the transfer of electricity, and the appearances were very remarkable; effervescence ensued at the positive pole, and, at the negative, there appeared small and brilliant globules of a perfectly metallic appearance, but which presently burned upon exposure to air, and seemed to reproduce the alkali. There now could be little doubt that this matter was the *base* of potassa; but it became necessary to collect and preserve it for examination; and this was a task attended by many serious and apparently insurmountable obstacles, for the globules were successively immersed in a great variety of fluids, upon all of which they had more or less action, and none of which afforded a means of retaining them in a metallic state; at length the fluid called *naphtha* was successfully employed, and in it they were collected and preserved for a considerable time without material alteration. They were found truly metallic, eminently combustible, remarkably light, acting energetically and inflaming upon water, and producing potassa by their union with oxygen. Many of their other properties were also determined; and it here deserves especially to be mentioned, that although *potassium*, for so this new metal was called, was only obtained in minute atoms, and a few grains in weight, all its essential properties, as subsequently determined, were correctly and minutely made out. *Sodium* was next obtained from soda by the same new method of decomposition; and shortly after the alkaline earths were shown to contain analogous inflammable and metallic bases. The *Philosophical Transactions* for several subsequent years contain continuations of these inquiries, which were actively and successfully pursued by their author, and which speedily attracting the admiration of the scientific world, induced others to resume and extend them.

In the year 1810 the subject of Sir HUMPHRY'S Bakerian Lecture is the "Oxymuriatic acid and its compounds," a subject which is pursued in several successive communications, abounding in original views and new discoveries. It is in these papers that the true nature of oxymuriatic

acid is demonstrated, that the views of SCHEELE respecting it are established, and that the erroneous reasoning regarding its composition, originating with BERTHOLLET, and sanctioned by the assent of the chemists of Europe, is refuted and subverted. Much acute reasoning, and many specimens of the true logic of the science, are to be found in these details, blended with sound descriptions of new compounds, and new applications of the facts that were developed: it is here that the nature of the muriatic acid is first demonstrated; that oxymuriatic acid (under the new name of *chlorine*) is shown to be an undecomposed substance; that a multiplicity of erroneous views respecting their compounds are corrected, and others established upon the basis of experiment, to the exclusion of hypothetical reasoning. The new theory to which these inquiries led, was actively canvassed and opposed; but the objections urged against it necessarily yielded to the sound arguments and unequivocal experiments upon which it was founded, and the fame which the author acquired, by the gradual admission and general adoption of these new modes of reasoning and of research, was scarcely inferior to that which rewarded his more brilliant discovery of the alkaline bases. The several papers which follow this Lecture, and in which, among other subjects, the nature of *fluorine* and of *iodine* are discussed, may be considered as continuations and illustrations of the Bakerian Lecture, and they each contain further proofs of the inventive genius and talent of their author.

DAVY had now established himself as one of the first chemists of Europe: whether we found his claims to that distinction upon the number and importance of his original discoveries, or upon the profundity of his reasoning powers displayed in their applications, and stamping a peculiar character upon his inquiries. About this time he became desirous of embodying the results of his labors, and of displaying them in a more connected and systematic form, and, accordingly, in 1810, he published the first volume of his *Elements of Chemical Philosophy*, a work which, though it bears some marks of hasty composition, is abundant in evidence of the author's talent as an eloquent writer, a clear reasoner, and a shrewd and sagacious experimentalist. It is to be regretted that the second volume of this work never appeared; for although it be true that the first chiefly embraced those parts of the science which had been the particular objects of his successful studies, it cannot be doubted that his genius would have cast a new light upon the departments of chemistry with which he was less immediately intimate. His *Elements of Agricultural Chemistry* appeared shortly after the *Chemical Philosophy*; it is a work containing some new and useful facts and views, and is well adapted to the capacities of those whom he intended to instruct.

Sir HUMPHRY had now laid a secure and deep foundation of permanent eminence and imperishable reputation as a chemical philosopher of the first class; but whilst he was thus employed, he was at the same time reaping equally verdant, though less durable laurels, as a lecturer; his style was peculiar and impressive; his eloquence powerful and appropriate; his experiments brilliant and original; his reasoning refined and acute. But to dwell further upon this subject would lead me to biographical particulars respecting his connection with the Royal Institution,

and to details not immediately belonging to my present object, which I willingly, and, indeed, anxiously avoid, and turn with pleasure to his discovery of the SAFETY-LAMP.

The first paper in relation to this subject is printed in the *Philosophical Transactions* for 1815, and was followed by four communications bearing upon the same inquiry, the last of which was read to the Royal Society in January, 1817. These essays would alone characterize their author as a philosopher of no common stamp. Finding that flame would not recede through tubes of very small diameters, the idea occurred to him of constructing a lamp, the flame of which should have no connexion with the surrounding air, except by capillary tubes; and he inferred, from previous experiments, that such a lamp might safely be employed for the illumination of coal-mines infested with the explosive atmosphere commonly called *fire-damp*. He then endeavoured to ascertain the extent to which the tubes might be shortened without interfering with the principle of safety, and was thus led to cut them down till their transverse section became a series of fine meshes: this so closely resembled *wire-gauze*, that he was induced to try how far that tissue would prevent the passage of flame, and finding it effectual, he employed it in the construction of his lamp, and ultimately adopted the simple and efficient arrangement now in general and successful use. His researches respecting the nature of flame, and the temperatures at which combustion may, under various circumstances, be carried on, are parts of this general inquiry, and are not less ingenious than original.

Sir JOSEPH BANKS, who had been for so many years President of the Royal Society, died in June, 1820, and on the 30th of November following, Sir HUMPHRY DAVY succeeded to that high and honorable office. His *Discourses*, delivered on various occasions before that body, will give a fair idea of the general style of his eloquence and power in oratorical composition. He continued to contribute papers as heretofore, and some of them upon subjects of much interest, ably and philosophically discussed: among them, the essays on the modes of protecting the copper sheathing of ships deserve especial notice*.

In the course of the year 1827, Sir HUMPHRY's general state of health became much impaired; he passed the greater part of the year 1828 in Italy, and terminated his memorable existence at Geneva, in May, 1829, in the fifty-second year of his age.

Of this eminent and extraordinary person two biographical memoirs have appeared, the one by Dr. PARIS, in 1831; and the other by his brother, Dr. JOHN DAVY, in 1836. Neither of these works will perhaps perfectly satisfy the *scientific* reader: they contain a variety of interesting and important matter, but are scarcely sufficiently ample in reference to those events in Sir HUMPHRY's life, principally connected with his chemical pursuits, and his philosophical eminence. Dr. DAVY has, however, to a considerable extent, filled this chasm in his brother's biography, by the recent republication of his *Life*, in the form of a prefatory memoir to Sir HUMPHRY's collected works. These volumes are a

* A list of Sir Humphry Davy's principal publications will be found at the end of Dr. Paris's work.

valuable addition to the philosophical literature of Europe, and furnish the chemical reader with a work of reference of great interest and usefulness.

I became acquainted with Sir H. DAVY very soon after his arrival in London in 1801, having been introduced to him as a boy fond of chemistry. I was at that time at Westminster School, and often stole away upon a half holiday, to pass an occasional hour at the Royal Institution; soon afterwards I went abroad, and as soon as possible after my return, I renewed my acquaintance with Sir HUMPHRY; this acquaintance ripened into the friendship which so long subsisted between us, and which ultimately led to an event of which I shall always be justly proud, that of having been recommended by himself as a proper person to succeed him as Professor of Chemistry in the Royal Institution; to which office, after having delivered a probationary course of lectures during the preceding spring, I was unanimously elected on the 7th of June, 1813. From the time that Sir HUMPHRY quitted England for the Continent, in October, 1813, till his return in 1815, and during his subsequent visit in 1818, till his return in 1820, he regularly corresponded with me; and in the intermediate periods I was almost constantly in the enjoyment of his friendship and his society, or a witness and occasional assistant in his experimental labors in the laboratory of the Royal Institution.

From this correspondence I have selected three letters, which may, I think, be interesting, as relating to some of the points touched upon in the preceding paragraphs:

My dear Sir,

Paris, *December 11, 1813.*

I shall enclose for the Royal Society a paper, containing results that, I think, will interest you. You will be so good as to give the paper to Sir Joseph as soon as you have perused it. I have sent him a copy, of which this is a duplicate. I wish that it may be read to the Royal Society as soon as possible. I transmit this copy to you, thinking that as you are preparing your Course, you will be glad to make an acquaintance with (iodine) a *fourth* supporter of combustion. Will you have the kindness to inform my brother of the contents of the paper; and request him to use some delicacy in communicating them to Dr. Hope, lest too great a shock should be given to the Professor, in finding the last hopes of oxymuriatic acid destroyed? I am only joking, for I know the Doctor is at the bottom too genuine a lover of science, and of truth, and of order, to preserve an arrangement which will have few advocates three months hence.

I leave Paris in a few days for Auvergne. You can write to me by the Transport Board on any matters of science, the letter being open, and sent under cover to Monsieur le Sénateur Comte Real, Bureau de Police, Paris. Kind remembrances to all friends. Lady Davy desires her best compliments.

I am, my dear Sir, very sincerely yours,

Wm. T. Brande, Esq., Secretary to the Royal Society,
Royal Institution, 21, Albemarle Street, London.

H. DAVY.

His next letter is written soon after his arrival in Italy, in 1818.

My dear Sir,

Idria, *August 23, 1818.*

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Since I wrote to you, at Vienna, we have made a very long journey. I have visited the most interesting parts of Hungary, Styria, Saltzbourg, and Carinthia, and have seen some mountain scenery quite as worthy of admiration as any I

ever saw in the Swiss Alps. I have lived amongst mountaineers purer and more uncorrupted than even the Swiss. We have had delightful weather, and have had full enjoyment of summer, fine but not sultry, in districts where, without fine weather, there could have been but little pleasure.

I will not write a geological letter, or describe to you the great calcareous mountain-chain that runs from Kevnoud, in Hungary, to Berchtesgarten in Bavaria, and to the centre of Carniola, with its belts of breccia, its intersections of schist, and its central column of granite. * * * * * But I will give you a line on the *quicksilver mines*, which I came here to see. The formation is in bituminous schist, which sometimes emits inflammable air, and which alternates with limestone, like the Derbyshire. I have this day been down 1120 feet, and returned without being *salivated*. I pity the poor workmen, who all lose their teeth in a very short time. The veins of cinnabar are very beautiful; and one I saw nearly a foot in thickness. My wife went down with me, and visited the whole mine, which is rather a feat to be talked of for a lady.

I found a great deal of inflammable air (Carburetted Hydrogen) in the great salt mine at Helstedt; the salt, like the quicksilver here, is in bituminous schist. I taught them the use of the lamp, which, notwithstanding the science of their imperial proprietor, they were still unacquainted with. A good many men had been burned a few months ago. The inflammable air is found in largest quantities where the *blue* salt is. I have been again searching in vain for the cause of this extraordinary colour.

I sent, in a letter to Mr. Hatchett, a little of Professor West's new metal, *Sirium*: I doubt its being a simple substance; perhaps you will try a few experiments upon it. I believe I mentioned to you, in my last letter, Count Stadion's *Oxychloric acid*; a very curious substance, very like sulphuric acid, and containing much more oxygen than Gay Lussac's acid. I have used detonating powder for Rivière's gun, made with the *oxychlorate* of Potassa, to use Stadion's name, and it answers perfectly. I am now in the *Proteus* country, and hope to send Sir Everard Home some alive; I go to the caverns where they are found, the day after tomorrow. I have seen nothing, and heard nothing, from England for two months. Pray address to me, Rome. I shall probably be there by the middle of October, on our way to Naples.

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I am, my dear Sir, very sincerely yours,

Wm. Thos. Brande, Esq., Sec., R.S.
Royal Institution, Albemarle Street, London.

H. DAVY.

The third letter was written shortly previous to his return to England, and to the death of Sir JOSEPH BANKS, who expired at his villa at Spring Grove, near Isleworth, on the 19th June, 1820.

Hotel de la Paix, Rue de la Paix, Paris, *May 20, 1820.*

My dear Sir,

It is long since I have written to you, but unless I have something to communicate, I do not like to trouble my friends; and in Italy, unless I rung changes upon my own small stock of scientific results, I had nothing to state in the way of chemical or philosophical information.

Here, there is little going on which you will not have seen noticed in the journals. A subject which seems to awaken much attention, is the increase of temperature of the surface of the globe, at considerable depths. If the results can be depended on, and are not influenced by accidental causes, the geometricians say they prove that at a few miles below the surface, the interior must be intensely hot; of a temperature far beyond that produced in any of our artificial operations. The subject is, at all events, a very curious one, and, in its geological relations, worth a very minute investigation.

Lord and Lady Spencer are here, and will be here for some time; they this morning gave me a piece of news which I hope is incorrect, but which makes us all very uneasy: it is that Sir Joseph is going to resign the chair of the Royal Society. * * * * * Pray write me a few lines, to tell me if this be true. Feeling very much interested in the progress of science in Great Britain, and in the dignity of

scientific men, and of the Royal Society, I shall deeply regret such a measure, if it be in contemplation. * * * * * From the way in which Lord Spencer expressed himself, I have no doubt he would accept the chair; at the same time, I did not put the question to him, but Lord Spencer, or * * * * * would give dignity to the situation; and scientific *Vice Presidents*, might keep alive the scientific character of the body. * * * * * Pray write to me by return of post upon this subject, which I think is almost a *national one*.

I am much obliged to you for your *Manual*, which is the best collection and arrangement of chemical science existing. I have given the only copy I have received, to Sementini, who is going to publish immediately an Italian translation of it. I preferred making it subservient to the progress of science, to keeping it for my own gratification. Lady Davy joins me in kind remembrances to Mrs. Brande.

Believe me to be, my dear Sir, very sincerely yours,

Wm. Brande, Esq., Sec. R.S., &c.

H. DAVY.

Royal Institution, Albemarle Street, London.

Of Sir HUMPHRY's latter days, the following particulars are extracted from the interesting narrative of his friend and physician, Dr. TOBIN, who accompanied him on his last journey into Italy, and was with him till his death. Dr. TOBIN says, that on his arrival in London, March 26, 1828, he found Sir HUMPHRY much altered during the four years which had elapsed since he last saw him, and it was evident that although his mind was still vigorous and full of energy, his bodily infirmities pressed heavily upon him. On the morning of the 29th of March, he left his house in Park Street, Grosvenor Square, for Dover, crossed next day to Calais, and then proceeded up the Rhine, and through Styria and Carniola, into Italy. He arrived at Rome on the 18th of November, without any remarkable change in his health. And, as it appears from Dr. TOBIN's narrative, that he frequently was occupied during the greater part of the day in fly-fishing and shooting, his corporeal strength must have been considerable. He, however, shunned society, and passed his evening, and such days as he kept the house, in being read to, and in playing at *écarté*, and dictating his *Vision*. In his diary, for instance, on the 31st of December, 1828, Dr. TOBIN says, "Our daily life has hitherto been as monotonous as possible. Sir Humphry sees no society, and wishes to see none, and his only pleasure and amusement seems to consist in shooting. He drives out every day in the surrounding *Campagna*, often to a distance of twelve or fourteen miles from Rome, when he gets out, and rides on his pony over the fields in search of quails or snipes. On his return, when he is not too much fatigued, he dictates to me a continuation of his *Vision*, which he thinks of forming into a series of dialogues on religion and other subjects; and our evenings are spent as they have been ever since we left Calais, with a game or two at cards, and with my reading to him different works, principally English and French, which he procures from a circulating library in the Corso. I have formed no acquaintances, as Sir Humphry wishes me not to do so; but when I have copied off the morning's dictation, I often take a solitary walk in the garden of the Pincio, to St. Peter's, or to the Colosseum." (TOBIN's *Journal*, p. 196.)

On the 20th of February, 1829, Sir H. DAVY was attacked with a renewed stroke of palsy*, which had nearly proved fatal, and which

* The first symptoms of this disease | 1826, and to have appeared after his
seem to have alarmed him in the year | exertions on the 30th of November in

induced Dr. TOBIN to write to Dr. DAVY at Malta, and to Lady DAVY in London; the former arrived at Rome on the 15th of March, and the latter on the 30th. By this time Sir HUMPHRY had considerably regained the power over his limbs, and was able to lie upon the sofa the greater part of the day. "It seems impossible," says Dr. TOBIN, "for him to exist without being read to, and on one day I read Shakspeare to him for *nine* hours."

On the 30th of April, Sir HUMPHRY, now accompanied by his wife and brother, left Rome, and passing through Sienna, Florence, Genoa, and Turin, over Mount Cenis, reached Geneva on the 28th of May; on the 29th, the following is recorded in Dr. TOBIN's *Diary*. "I quitted Sir Humphry yesterday evening, after having read to him as usual till about ten o'clock. Our book was Smollett's *Humphrey Clinker*, and little did I think it was the last book he would ever listen to. He seemed in tolerable spirits, but upon going to bed was seized with spasms, which however, were not violent, and soon ceased. I left him when in bed, and bidding me 'good night,' he said I should see him better in the morning. Lady Davy and the Doctor also quitted him, and George (his servant) went to bed in his master's room, as he always had done since Sir Humphry's illness at Rome. At six o'clock this morning, Lady Davy's man-servant came to my room, and told me that Sir Humphry was no more! I replied that it was impossible, and that he probably only lay in a torpor; but I went down to his room instantly, when I found that the servant's words were, alas! but too true. I asked George why he had not called me, when he said, that he had sent up, but now found that it had been to a wrong room. He told me that Sir Humphry went to sleep after we had left him, but that he twice waked, and that at half-past one, hearing him get out of bed, he went to him, when Sir Humphry said he did not want his assistance, and poured some solution of acetate of morphine into a wine-glass of water; but this still remained untouched upon his table. George then helped him into bed, where he says, he lay quite still till a little after two o'clock, when hearing him groan, he went to him, and found that he was senseless and expiring. He instantly called up Lady Davy and the Doctor, and sent up, as he believed, to me; but Sir Humphry, he says, never spoke again, and expired without a sigh.

"I had so often, whilst at Rome, seen Sir Humphry lie for hours together in a state of torpor, and to all appearance dead, that it was difficult for me to persuade myself of the truth; but the delusion at length vanished, and it became too evident that all that remained before me of this great philosopher, was merely the cold and senseless frame with which he had worked. The animating spirit had fled to its oft self-imagined planetary world, there to join the rejoicing souls of the great and good of past ages, soaring from system to system, and with them still to do good in a higher and less bounded sphere, and I knew that it was freed from many a wearisome and painful toil. Yet I could

that year, on which occasion he delivered his last discourse, at the anniversary meeting of the Royal Society; and some weeks afterwards, whilst upon a shooting	excursion with Lord Gage, in Sussex, he was seized with a more alarming attack, from the immediate effects of which he however soon rallied.
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not look upon Sir Humphry as he was, without remembering that which he had been, and my tears would fall, spite of my effort to restrain them."

The following memorandum, relating to the last hours of his brother's life, is given by Dr. DAVY (*Memoirs*, vol. ii., p. 365): "On the 28th of May, 1829, we arrived at Geneva: at five, he dined at table and made a tolerable dinner; after dinner he was read to, according to custom. At nine o'clock, he proposed to go to bed. In undressing, he struck his elbow against the projecting arm of the sofa on which he sat; the effect was very extraordinary; he was suddenly seized with an universal tremor; he experienced intense pain in the part struck, and a sensation, he said, as if he were dying. He was got into bed as soon as possible. The painful sensations quickly subsided, and in a few minutes were entirely gone. There was no mark of hurt of the elbow, no pain, or remaining tenderness; and the effect of the blow perplexed him no less than it did me: a slight feverish feeling followed, which he thought little of; he took an anodyne draught of acetate of morphia, and then desired to be read to, that he might be composed to sleep by agreeable images.

"About half-past nine he wished to be left alone, and I took my leave of him for the night, and for ever on earth. His servant, who always slept in his room, called me about half-past two, saying he was taken very ill. I went to him immediately; he was then in a state of insensibility; his respiration extremely slow and convulsive, and the pulse imperceptible: he was dying; and in a few minutes he expired. I thank God I was present to close his eyes. In death, his countenance was composed, and of its mildest expression, indicative of no pain or suffering in the separation of the immortal from the mortal part. This fatal moment was about three A.M. on the 29th of May." His remains were deposited on the 1st of June in the burying-ground without the walls of Geneva, and close to the grave of Professor PICTET.

The theory of definite proportionals was adopted and illustrated by Sir H. DAVY, and his *Elements* is the first publication in which it was generally applied. This theory received, about the same time, extensive elucidation at the hands of M. GAY LUSSAC, but its promulgation in this country is chiefly to be attributed to Dr. WOLLASTON, whose admirable suggestion of a synoptic scale of chemical equivalents, already referred to, was brought before the Royal Society in November, 1813. Many years previous to this he had established the important doctrine of multiple proportions, in a paper "On Super-acid and Sub-acid Salts," printed in the *Philosophical Transactions* for the year 1808: he now showed the important practical applications of which the theory was susceptible, and by connecting the scale of equivalents with GUNTER's sliding rule, has put into the hand of the chemist an instrument infinite in its uses, and equally essential to the student, the adept, and the manufacturer.

Dr. WOLLASTON's first contribution to the Transactions of the Royal Society was in June, 1797, being an essay *On Gouty and Urinous Concretions*, in which he made known several new compounds connected with the production of those maladies, in addition to the uric combinations previously discovered by SCHEELE: these were, Phosphate of Lime;

Ammonio-magnesian Phosphate; a mixture of the two, forming the *fusible* Calculus; Oxalate of Lime; and, more lately, he added Cystic Oxide to the list of his previous discoveries. (*Phil. Trans.*, 1810.) In 1804 and 1805, he made known Palladium and Rhodium, two new metals contained in the ore of platinum, and associated with Osmium and Iridium, discovered about the same time by TENNANT. In 1809, he showed that the supposed new metal, Tantalum, was identical with Columbium, previously discovered by HATCHETT; and shortly before his death, which happened on the 22d of December, 1828, in the sixty-third year of his age, he transmitted to the Royal Society the *Bakerian Lecture*, in which he fully describes his ingenious method of rendering platinum malleable.

Dr. WOLLASTON made a few other chemical communications to the Royal Society, but his papers are chiefly on subjects more immediately connected with physical and physiological inquiries: they are all remarkable for the singular and satisfactory simplicity of his experimental methods, for the perspicuity of his theoretical deductions, and for the extreme caution with which he touches upon generalizations and hypothesis. His uncommon tact, neatness, and dexterity as an experimental chemist, will never be forgotten by those who had an opportunity of witnessing his performance of any analytical operation; he practised a peculiar method of microscopic research, in which he willingly instructed those who asked his information; and we owe to him numerous abbreviations of tedious processes, and a variety of improvements in the application of tests, which have gradually become public property, although he never could be induced to describe his manipulations in print, or to communicate to the world his happy and peculiar contrivances.

Of Dr. WOLLASTON, (who was born at East Dereham, in Norfolk, on the 6th of August, 1766,) no authentic biography has yet appeared; the following are a few memoranda respecting his last illness, which were obtained from conversation, at the time, with some of his intimate friends.

In October, 1827, while accompanying a friend to Cashiobury, the seat of the Earl of Essex, he spoke of a numbness which he had for some time felt in his left arm, and which he stated he considered as a symptom of paralysis, a disease to which his father and eldest brother had fallen victims, and of which, at a subsequent period, another brother also died. In June, 1828, while on a fishing excursion at Stockbridge, feeling some stronger premonitory indications of a paralytic seizure, he abruptly quitted his amusement, and returned to London. In July of the same year, while on a visit to the late Earl Spencer, at the Isle of Wight, he noticed that a part of the retina of his left eye had become insensible to the action of light. In the month of September, he went upon a shooting excursion to Mr. Whitbread's in Bedfordshire, where he remained eight days, and enjoyed his sport: one evening he jokingly said, "For the first time in my life I count my game by the quarter of a hundred," having killed twenty-five head. He returned home better in health; but soon after, the sensation in his arm became worse, and whilst staying with Mr. Blake in Hertfordshire, he felt so unwell and uncomfortable, as to be obliged to return home a day or two earlier than he intended. In the

course of the following week, symptoms more decidedly alarming, came on; the use of his arm was much impaired, and the muscles of the face and organs of speech were affected: his mental faculties, however, remained entire to the last. He was sedulously attended by several medical friends, and especially by Dr. JAMES SOMERVILLE, who remained in the house during his illness, and until his death.

The loss of two such men as WOLLASTON and DAVY, within so short a period, and scarcely beyond the prime of life, was a serious national calamity: the sketch which I have given of their labors is a most imperfect outline; but it would have been improper and indecorous to have dismissed this brief History of Chemistry without such notice, and I shall conclude with the following delineation of their intellectual portraits, for which we are indebted to the late Dr. HENRY. (*Elem. of Chem.*, 11th edit., viii.)

“To those high gifts of nature, which are the characteristics of genius, and which constitute its very essence, both those eminent men united an unwearied industry and zeal in research, and habits of accurate reasoning, without which even the energies of genius are inadequate to the achievement of great scientific designs. With these excellencies, common to both, they were nevertheless distinguishable by marked intellectual peculiarities. Bold, ardent, and enthusiastic, DAVY soared to greater heights; he commanded a wider horizon; and his keen vision penetrated to its utmost boundaries. His imagination, in the highest degree fertile and inventive, took a rapid and extensive range in pursuit of conjectural analogies, which he submitted to close and patient comparison with known facts, and tried by an appeal to ingenious and conclusive experiments. He was imbued with the spirit, and was a master in the practice, of the inductive logic; and he has left us some of the noblest examples of the efficacy of that great instrument of human reason in the discovery of truth. He applied it, not only to connect classes of facts of more limited extent and importance, but to develop great and comprehensive laws, which embrace phenomena that are almost universal to the natural world. In explaining those laws, he cast upon them the illumination of his own clear and vivid conceptions; he felt an intense admiration of the beauty, order, and harmony, which are conspicuous in the perfect CHEMISTRY of NATURE; and he expressed those feelings, with a force of eloquence, which could issue only from a mind of the highest powers, and of the finest sensibilities. With much less enthusiasm from temperament, Dr. WOLLASTON was endowed with bodily senses of extraordinary acuteness and accuracy, and with great general vigour of understanding. Trained in the discipline of the exact sciences, he had acquired a powerful command over his attention, and had habituated himself to the most rigid correctness, both of thought and language. He was sufficiently provided with the resources of the mathematics, to be enabled to pursue, with success, profound inquiries in mechanical and optical philosophy, the results of which enabled him to unfold the causes of phenomena, not before understood, and to enrich the arts, connected with those sciences, by the invention of ingenious and valuable instruments. In Chemistry, he was distinguished by the extreme nicety and delicacy of his observations; by the quickness and precision with which he marked resemblances, and

discriminated differences; the sagacity with which he devised experiments, and anticipated their results; and the skill with which he executed the analyses of fragments of new substances, often so minute as to be scarcely perceptible by ordinary eyes. He was remarkable, too, for the caution, with which he advanced from facts to general conclusions; a caution which, if it sometimes prevented him from reaching at once to the most sublime truths, yet rendered every step of his ascent a secure station, from which it was easy to rise to higher and more enlarged inductions."

The talented author of the preceding paragraph is himself now amongst those who claim a place in this historical outline of the progress of chemical philosophy. In the address delivered at the Anniversary Meeting of the Royal Society, on the 30th November, 1836, the President says, "The last name which occurs in the melancholy list of our departed associates is that of Dr. WILLIAM HENRY, to whom the science of Chemistry generally, and of Gaseous Chemistry in particular, is under great obligations. He was the author of nine papers in our *Transactions*, many of them of great merit; and his *Elements of Chemistry* is one of the best-written and best arranged compendiums of that important and extensive science which has been published of late years, whether in our own or in any other language. The *Memoirs* of the Manchester Society are chiefly indebted to him, in conjunction with Dr. DALTON, for the high character which they have so long maintained. Dr. HENRY, like Dr. WOLLASTON, made the results of science, obtained by the most original and difficult researches, the foundation of a splendid fortune; and few persons have contributed more effectually by their discoveries and exertions to the promotion of those arts and manufactures which form the foundation of the prosperity of a great commercial nation."

PART I.

THE POWERS OF MATTER,

AND THE

NON-METALLIC ELEMENTS.

A MANUAL OF CHEMISTRY.

CHAPTER I.

HOMOGENEOUS ATTRACTION. CRYSTALLIZATION.

IT is the object of Chemistry to discover the composition of the varieties of matter and to investigate the causes and effects of all changes in their constitution, whether produced by heat, mixture, or other means. The general range, therefore, of this science is so extensive, and the individual cases requiring explanation so numerous, that *Arrangement* is of much consequence to its successful study. In the present state of our knowledge, it appears most convenient to begin with the discussions relating to the *general powers and properties of matter*, and afterwards to proceed to the examination of *individual substances*, and to the phenomena which they offer when presented to each other under circumstances favourable to the exertion of their mutual chemical agencies.

The powers and properties of matter, connected with chemical changes, may be considered under the heads of Homogeneous Attraction, or Aggregation; Heat; Light; Heterogeneous or Chemical Attraction, or Affinity; Electricity, and Magnetism.

§ 1. ATTRACTION. AGGREGATION. CRYSTALLIZATION.

ATTRACTION may be regarded as acting at *sensible* and at *insensible* distances. In the former case, it is called *gravitation*. It is the power by which substances are propelled towards the earth; it exists in all known forms of matter; it acts directly as the mass, and inversely as the square of the distance: restrained by *inertia*, it preserves the planetary bodies in their orbits, presides over their movements, and tends to confer upon the system of the universe that consummate harmony which Newton first unveiled.

Attraction is also exerted at *insensible* distances, and among the atoms of matter. It thus preserves the form, and modifies the texture of solids; gives a spherical figure to fluids; causes the adhesion of surfaces; and influences the mechanical characters of bodies. The different forces with which it is exerted are seen in the different qualities of solids, which are sometimes exceedingly hard and difficultly divisible, as diamond, rock-crystal, &c.: others are comparatively soft or brittle, and exhibit less intensity of aggregation, such as calcareous spar, chalk, &c.: and in others the power is so modified as to produce plasticity, porosity, elasticity, and tenacity, as seen in clay, sponge, caoutchouc, and iron.

As gravitation is counteracted by inertia, so is aggregation opposed by *heat*; and it is probable that the different states or forms of matter are chiefly dependent upon the relative intensities of these antagonist forces. In *solids* aggregation predominates so as to prevent their particles freely moving upon each other; but in fluids they move upon each other with the utmost ease, and in some more readily than in others; hence their division into *liquids or inelastic fluids*, and *aëriiform or elastic fluids*.

The dimensions of liquids are not materially influenced by pressure; they were, indeed, for a long time considered as absolutely inelastic and incompressible; this, however, is not strictly true, although the force required to change their volume is great, and the extent of the change small. The following table shows the amount of compression of four liquids, deduced from the experiments of Oersted, in millionths of their volume, for each additional atmosphere.

Mercury.....	2·65 millionth parts.		Water	46·65 millionth parts.
Alcohol	21·65 ,,		Ether.....	61·65 ,,

By plunging a vessel of water into the sea to a depth of 1000 fathoms, the compression is said to amount to one-twentieth of the bulk. In all cases after the pressure is withdrawn, the liquids reassume their original bulks.

The permanent gases appear to be indefinitely elastic and compressible, their volume, as was first accurately ascertained by Mariotte, being inversely as the pressure; so that supposing 100 volumes of atmospheric air under a pressure of 100 pounds to be subjected to the pressure of 200 pounds, its bulk would be reduced to 50 volumes, and augmented to 200 volumes under a pressure of 50 pounds. (See ATMOSPHERIC AIR.) But although this law holds good in respect to atmospheric air and its components, and to such gases as have not been coerced into liquids, it fails with respect to the latter, especially when they approximate liquefaction: thus if we compare air with sulphurous acid, the volumes under equal pressures will be as follows.

Air.	Sulphurous Acid.	Air.	Sulphurous Acid.
1000	1000	559	554
853	851	314	301

It is therefore not improbable, that every aëriform fluid, under adequate pressure, would exhibit similar irregularities, inasmuch as it is probable that, under such circumstances, each would ultimately become liquid.

The influences of *heat* upon matter will be fully discussed in the section upon that subject.

The mutual attraction between the *surfaces* of solids and liquids gives rise to the phenomena of *capillary attraction*, so called from its causing the visible rise of fluids in tubes of small bore: thus, if a tube, with a capillary bore of one-fiftieth of an inch, be dipped at one end into a glass of water, the water rises to about $2\frac{1}{2}$ inches, and the rise is great in proportion to the smallness of the bore. If two plates of perfectly clean glass be so held as to form a very acute angle with each other, and their lower edges be then dipped into water, the liquid rises in the form of a curve (hyperbola) between the plates, rising highest where the space between them is least. It is in consequence of this species of attraction that a drop of water upon a solid surface wets and adheres to it; and that the surface of the water in a clean tumbler is not truly level, but a little elevated upon the edges. These phenomena depend upon the nature of the substances presented to each other; thus water will not rise upon greasy glass, or wax; and hence also different liquids rise to different heights in the same tube, independent of their specific gravities, and of their relative degrees of viscosity; and mercury not only does not rise, but is depressed in the bore of a common glass tube: so that, unlike water, it presents a convex instead of a concave surface when poured

into a glass, because the attraction of the particles of the mercury for each other is great, and they are not attracted by those of the glass; in other words, they are incapable of *wetting* it. “The mercury within the tube is cut off by the inactive surface of the glass from the homogeneous attraction of the surrounding mass; its own self-attractive force therefore acts as from its centre, drawing its particles together and causing them to assume more or less of a globular aggregation, according to the same law which determines the spheroidal form of a suspended drop of liquid.” (DANIELL’S *Introd.*, § 83.) The rising of fluids in porous and spongy bodies, the ascent of oil or spirit in the wicks of lamps, the diffusion of moisture in the earth, and the distribution of the juices of plants, are a few of the important consequences of capillary attraction.

A similar adhesive attraction takes place also between solids and aëriform bodies, as is illustrated by the following experiments. Sift some magnesia upon the surface of water, and it will presently sink to the bottom; sift in the same way some fine iron filings, and although their specific gravity is nearly four times greater than that of magnesia, and between seven and eight times greater than that of water, they float upon the surface, and to such an extent, that a stratum of considerable thickness may be laid on the liquid; this at length sinks in considerable masses, when it is seen that they had been previously buoyed up by the adhesion of air, which their accumulated weight even carries with them to the bottom, the surface of each fragment of metal having been enfilmed with air, which prevented its being wetted by the water: in the case of the magnesia, its attraction for air being less, it was more easily displaced by the water. The force of adhesion of air to glass is also considerable, and to this cause Daniell refers the gradual deterioration of barometers by the creeping up of air between the mercury and the tube, an effect which he ingeniously prevented by welding a ring of platinum to the bottom of the tube, which admits of being *wetted* by the mercury, and so intercepts the ingress of the air. The welding of the platinum to the hot glass is, he observes, a good instance of strong heterogeneous attraction. (*Introd.* § 87.)

The adhesion of air to a liquid is shown by the quantity which escapes when water is poured from one vessel into another, the air attached to its surface being carried down by the momentum of the falling mass and again escaping in bubbles: the foam of water-falls results from the same cause, and it is thus that air gradually pervades masses of water, and tends to its entire aëration, so as to fit it for the respiration of aquatic animals, and for the sustenance of vegetable life. This air escapes under diminished pressure, and may be entirely expelled by long-continued boiling.

The results of attraction, as relating to the shape and form of matter, are, in many cases, much influenced by the circumstances under which it has taken place: sometimes the particles are, as it were, indiscriminately collected; at others, they are symmetrically arranged, producing regular and determinate figures; in this case, bodies of the same composition often affect the same form; hence we are not unfrequently enabled to infer the composition of a substance from accurate inspection of its mechanical characters.

Identity of form, however, is not necessarily associated with identity of composition, for certain substances may be substituted for each other in combination, without affecting the form of the compound. Thus the arseniate and binarseniate of soda have the same forms as the phosphate and biphosphate of soda; and the arseniate and binarseniate of ammonia resemble the phosphate and biphosphate of that alkali. Professor Mitscherlich, (*Ann. Ch. et Ph.*, xiv. xix. xxiv.) to whom we owe these and other facts connected with the subject which we shall consider afterwards, terms such salts *isomorphous*, and has shown that there is a remarkable analogy in the chemical arrangement of their constituents. Thus, in the above instances, the equivalents of acid, base, and water of crystallization, correspond; and he has traced a similar correspondence in the atomic constitution of the acids and bases of the salts. Thus the arsenic and phosphoric acids each include two equivalents of base and five of oxygen, and are therefore themselves isomorphous; so also phosphorus and arsenic are presumed to be isomorphous, isomorphous compounds in general appearing to arise from isomorphous elements. So also in respect to the isomorphism of the sulphates, seleniates, chromates, and manganates of the same base, each of the *acids* in these cases containing three atoms of oxygen to one of sulphur, selenium, &c. In respect to *bases*, similar analogies are observable: thus the salts formed by magnesia, the protoxides of zinc, iron, nickel, cobalt, and copper, with a common acid, are isomorphous; and alumina and the sesquioxides of chromium, manganese, and iron, each of which contain two atoms of base and three of oxygen, replace each other in many combinations without change of crystalline figure, as is especially well illustrated in some of their double salts.

In reference to this definition of the term *isomorphism*, the following tabular view of certain "isomorphous groups" will be intelligible.

Chlorine	}	Chloric acid.....	Cl O ₅	Potassium	}	Their protoxides.	K O
Iodine		Iodic acid	I O ₅	Sodium			Na O
Bromine		Bromic acid.....	Br O ₅	Ammonium			NH ₄ O
Sulphur	}	Sulphuric acid....	S O ₃	Calcium	}	Their protoxides.	Ca O
Selenium		Selenic acid.....	Se O ₃	Magnesium			Mg O
				Manganese			Mn O
				Iron			Fe O
Phosphorus	}	Phosphoric acid .	P ₂ O ₅	Zinc			Zn O
Arsenic		Arsenic acid	As ₂ O ₅	Cadmium			Cd O
				Cobalt			Co O
				Nickel			Ni O
Barium	}	Their protoxides.	Ba O	Aluminum	}	Their sesquioxides.	Al ₂ O ₃
Strontium			Sr O	Manganese			Mn ₂ O ₃
Lead			Pb O	Iron			Fe ₂ O ₃
				Chromium			Cr ₂ O ₃

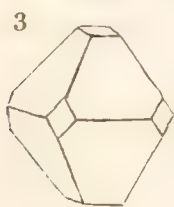
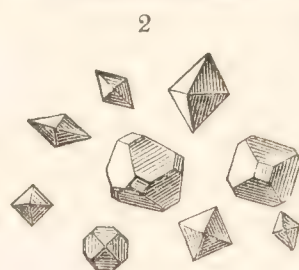
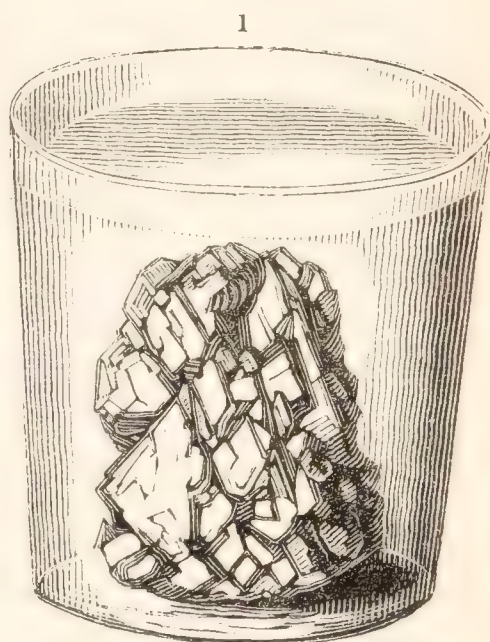
The further details respecting the analogies prevalent among these groups and their respective combinations, will be found under the history of the individual compounds.

The regular polyhedral solids resulting from homogeneous attraction are usually called *crystals*; and the bodies are said to be susceptible of *crystallization*. To enable the particles of bodies to assume that symmetry of form which crystals exhibit, it is obvious that they must have freedom

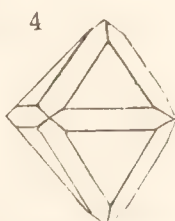
of motion; and, accordingly, the first step towards obtaining a body in its perfect crystalline state, is to confer upon it either the form of liquid or vapour, as by solution in water or other liquid, or by the application of heat.

When common salt is dissolved in water, its particles may be regarded as disposed at regular distances throughout the fluid; and if the quantity of water be considerable, the particles will be too far asunder to exert reciprocal attraction: in other words, they will be more powerfully attracted by the water than by each other. If we now slowly get rid of a portion of the water by evaporation, some of the saline particles will gradually approach and aggregate according to certain laws, producing a regular solid of a *cubic form*; another portion of the salt will remain dissolved in the residuary water, which is usually called the *mother liquor*.

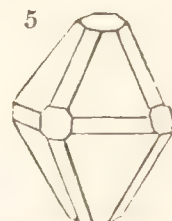
When certain crystallized substances are slowly acted upon by water, its influence is often curiously modified by the texture of the saline mass. (DANIELL, *Quart. Journ.*, I.) If for instance, a shapeless lump of alum be immersed in cold water, in a few days the surface of the salt will be eaten and carved out into a variety of regular forms, somewhat as represented in the annexed cut. If we now put a drop of the solution upon a plate of glass, as the water slowly evaporates, the particles of alum which it contained congregate into regular forms, which, when examined by a lens, appear as in fig. 2, and are small eight-sided figures, or *octohedra*. In this case the water is said to be the *solvent* of the alum, and the process by which it is obtained in regular forms or *crystals*, is called *crystallization*. In this and similar instances, the crystals are liable to certain *modifications*; thus, among the small octohedrons, to which we have adverted, it is not uncommon to find some, the *angles* of which are cut off, or *truncated*, or replaced by secondary surfaces; sometimes the *edges* too are similarly modified, and the crystals assume these figures:



Truncated Angles.



Truncated Edges.



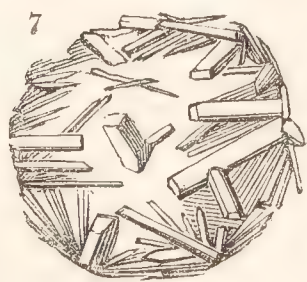
Truncated Edges and Angles.

Most of the saline substances soluble in water may be thus exhibited in a crystalline form; and as each substance usually assumes a distinct figure, or is characterized by some obvious, and, at the same time, peculiar properties, we are often enabled to pronounce upon the chemical nature or composition of a body, by a careful examination of its crystalline forms; and such experiments are particularly neat and satisfactory, in consequence

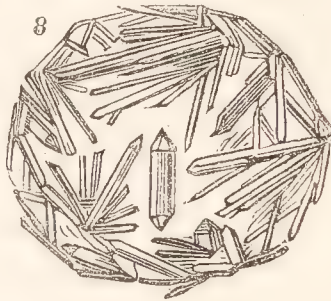
of their facility, and the small scale upon which they may be performed: for the figures of the smallest crystals obtained from a drop of their solution, resemble the large ones formed in gallons of it; and although, in collecting specimens of crystallized salts, it is convenient to have them large and perfect, the smallest ones that may be viewed through a microscope furnish the chemist with equally satisfactory evidence of the nature of the dissolved salt: for instance; put a tea-spoonful of common salt, nitre, Glauber's salt, and Epsom salt, into separate wine glasses: fill them up with water, and occasionally stir their contents to help the solution: when dissolved take a drop of the clear liquor, with a glass rod, out of each of the wine-glasses, and place them side by side upon a strip of clean glass, which may be placed upon a chimney-piece, or somewhere very gently warmed. As the water evaporates, the salts will crystallize, and we shall observe the following figures appropriate to each: the common salt exhibits *cubes*; the Epsom salt, *four-sided prisms*; the nitre *six-sided prisms*; the Glauber's salt, *striated six-sided prisms*.



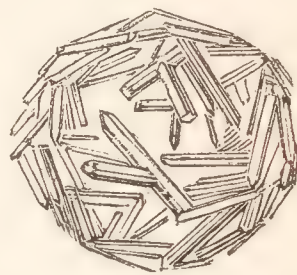
Common Salt.



Epsom Salt.



Nitre.



Glauber's Salt.

The Glauber's salt and the nitre might possibly at first be mistaken for each other, but, while the latter remains unaltered by exposure to air, the former soon loses its transparency, and crumbles down into white powder. Salts which behave thus are said to *effloresce**: other salts, instead of thus spontaneously parting with *water of crystallization*, attract moisture from the air, or *deliquesce*, as is the case with carbonate of potassa, acetate of potassa, chloride of calcium, &c.: alum and many other salts, although they contain water, do not thus part with it, and are *permanent* in the air. But water is not necessarily contained in all crystals: there is none, for instance, in nitre; and such are called *anhydrous salts*†. Some salts require a high temperature to deprive them of water. This is the case with gypsum, or sulphate of lime, which is frequently found in large transparent crystals, permanent in the air; but at a red heat they lose one-fifth their weight of water, and crumble down into the white powder commonly called *plaster of Paris*,

* This property of efflorescence would appear in some cases to depend upon superficial fracture, for Mr. Faraday found that crystals of carbonate, phosphate, and sulphate of soda, having no parts of their surfaces broken, and carefully preserved from external violence, remained perfect; but upon breaking or scratching their surface efflorescence began at that part, and covered the whole. *Phil. Trans.*, 1834, p. 74.

† It will afterwards be found that the proportion of water in hydrated crystals is *definite*, and that several salts form distinct

crystals with different proportions of water. (According to Longchamp, this water is only contained in the capillary cavities of the crystals. *Ann. Ch. et Ph.*, 3 Ser. vi. 19.) There are many salts which though they readily part with a portion of their component water, retain another portion with more or less obstinacy: this last frequently replaces bases, and has therefore been termed by Graham, *basic* or *constitutional water*: of these distinctions, the history of individual salts will furnish frequent instances. (See also MILLON. *Ann. Ch. et Ph.*, Feb., 1845.)

which is, therefore, an *anhydrous* sulphate of lime, and which, when mixed with a little water, again combines with it, and concretes in the act of combination; hence the use of this substance for forming casts or impressions, as seen in mouldings, busts, &c. Efflorescent salts may sometimes be conveniently preserved by slightly oiling their surfaces, or by soaking them for a few hours in olive oil, and then wiping them and putting them in bottles; or they may be kept under a glass shade in which is also included a small saucer of water. The action of heat upon salts is much influenced by their relative quantities of water of crystallization; it renders some of them, such as sulphate of soda, extremely fusible; from others the water evaporates before fusion, and occasions the efflorescence of the salt; and if contained in their pores, it causes them to *decrepitate*, or fly to pieces when heated, with a peculiar crackling; but this effect more generally depends upon the sudden expansion of the outer crust of the crystal, its peculiar texture, and its bad conducting power for heat, the most powerfully decrepitating salts being amongst those which are anhydrous.

The regular figures of crystals will be influenced by the rapidity of the evaporation; if the process be slowly conducted, the particles unite with great regularity; if hurried, the crystals are irregular and confused. Loaf-sugar and sugar-candy furnish good instances of such modifications; the former being the result of rapid, the latter of slow, crystallization. In common cases, the evaporation may be continued till a *pellicle* forms upon the surface of the solution, which indicates that the attraction of the saline particles for each other is becoming superior to their attraction for the water. The formation,

therefore, of a superficial pellicle is the common criterion of the fitness of a solution for crystallization; but where the object is to obtain very regular and large crystals, the evaporation must be slower, and carried to less extent; even *spontaneous evaporation*, or that which takes place at common temperatures, must be resorted to.

It is in this way that the large crystals of sulphate of magnesia and of nitrate of potassa, represented in figs. 10 and 11, were procured; they are here inserted to show the size and perfection of crystals thus slowly deposited in large quantities of their solutions, as contrasted with the microscopic forms described above.

There are certain bodies which may be dissolved or liquefied by heat,

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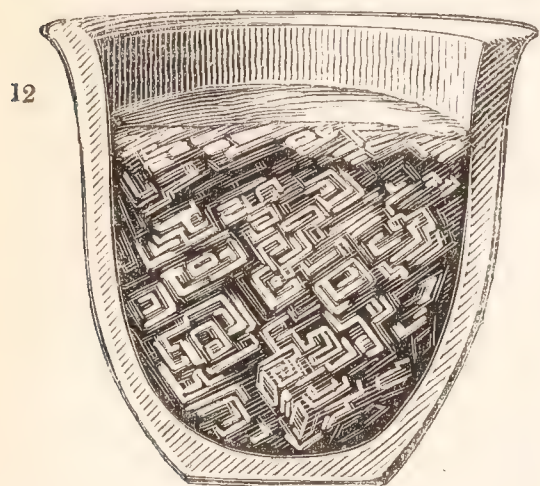
Epsom Salt, or Sulphate of
Magnesia.

11



Saltpetre, or Nitrate of
Potassa.

and, during slow cooling, may be made to crystallize. This is the case with many of the metals; and among them *bismuth* furnishes, when carefully managed, the most beautiful results; for this purpose a few pounds of it should be melted in a deep iron ladle or crucible, and, as soon as the

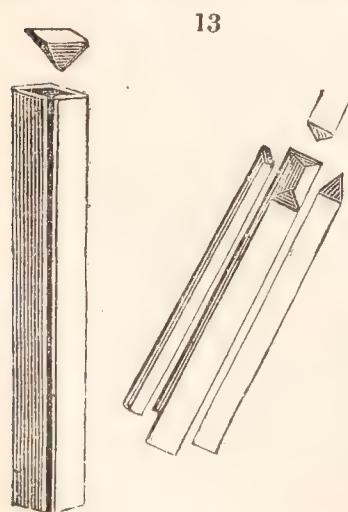


Crystallization of Bismuth.

surface has concreted, it should be punctured with a pointed iron rod, and the liquid metal immediately poured out from the interior; on cautiously breaking the hollow ingot thus obtained, the interior cavity will be found lined with dissected cubical crystals, fig. 12. *Sulphur* may be artificially crystallized by a similar process, and furnishes beautiful heaps of delicate prisms. The masses of crystallized *spermaceti*, often exhibited in shop windows, are obtained in the same way; and it is probable that the

cavities in rocks and veins, bearing marks of igneous fusion, and often lined with magnificent specimens of crystalline minerals, owe their origin to some analogous process.

There is another way of showing the crystalline texture of metals, which, with some of them, answers very well; it consists in washing over a thin plate of the metal with some acid which acts upon its surface. If tin-foil or tin-plate be thus washed over with dilute nitro-muriatic acid, the crystallization of the tin is often rendered beautifully manifest: this has been applied to ornamental purposes, under the name of *moirée metallique*, and different colours may be given to the surface by transparent varnishes. (See TIN.) Daniell also developed the crystalline texture of several of the metals by steeping masses of them in acids, by which their surfaces were carved out like the alum in water: and the crystalline structure of a bar of tin was beautifully shown by placing it horizontally in mercury and turning it frequently upon its different faces so as to insure uniformity of action; in about twenty-four hours fissures appear along its lateral and terminal edges which, by gradually splitting, resolve the bar into four equal trihedral rectangular prisms, which, as well as two pyramids from their extremities, may be separated from each other by the point of a knife: it is indifferent to this result whether the square form be given to the bar by casting, hammering, or the filing down of any



other shape. The annexed figures shew the lateral fissures and pyramid and the further separation into four trihedral bars. He further observes, in reference to this development of crystalline architecture, that "if a large crystal of sulphuret of antimony be introduced into a portion of fused sulphuret, and the heat be moderately continued, it will begin to melt down; but so far from this taking place uniformly at the surface, crystals will sometimes be left projecting half an inch from it; and in other places the cavities left by fused crystals will be so large and have such perfect surfaces that

their angles may readily be ascertained. In order to observe these phe-

nomena it is only necessary to remove the half-fused piece of sulphuret from its hot bath and allow it to cool."

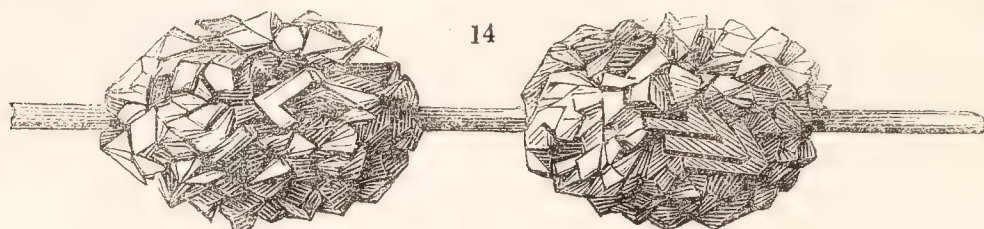
When bodies are raised in vapour, and this is again condensed into the *solid* state, the process is generally called *sublimation*, and is not uncommonly resorted to to obtain such volatile matters in the form of crystals. The appearance of *camphor*, when thus slowly sublimed, is often extremely beautiful; so also that of *benzoic acid*. *Iodine* is another body well calculated for the experiment; put a little of it into a clean Florence flask, and gently heat it; it will presently be converted into a deep violet vapour, which, subliming to the cold parts of the vessel, will there condense in small brilliant crystals of octohedral and rhomboidal figures. There is a substance called *naphthalin*, obtained during the distillation of coal-tar, and which may commonly be procured at gas-works: when pure, it is white and crystalline, and, if heated in a large phial or flask, its vapour congeals in lamellar crystals of extreme tenuity, crossing each other in all directions, and exhibiting a very singular appearance. *Calomel* and *corrosive sublimate* may be crystallized by a similar process, but the temperature required for their sublimation is considerable; and good crystals can only be obtained by operating upon large quantities, and subliming them very slowly. When flakes of *snow* are examined, they are found to be congeries of crystals of ice produced by the cooling of the vapour of water.

Some substances are so easily decomposed by heat, and at the same time retain water with such avidity, that it is impossible to crystallize them by the above processes: in these cases, crystallization may sometimes be effected by placing the solution under the exhausted receiver of an air-pump, over a surface of sulphuric acid, which, by absorbing the vapour as it rises, causes rapid evaporation at a low temperature.

Some salts may be brought to crystallize by the addition of substances having a strong affinity for water, by which its attraction for the dissolved matters is weakened: thus nitric acid added to a strong solution of nitrate of baryta throws down a crystalline precipitate of the salt; and alcohol, added to certain aqueous saline solutions, sulphate of soda and sulphate of magnesia for instance, produces a separation of crystals; but they are generally small and indistinct.

When two salts are present in the same solution, they often may be separated by crystallization, that which is least soluble constituting the earlier crop of crystals; or sometimes, one forms distinct groups upon the other; there are many salts which may in this way be entirely and effectually separated. This method, however, is ineffectual with most isomorphous salts, and with such as form double combinations. When, for instance, the *sulphates of iron and copper* are in solution together, crystals may be obtained of the same form as those of sulphate of iron, but containing variable proportions of sulphate of copper: in the same way the *sulphates of zinc and manganese*, and of *magnesia and manganese*, crystallize together. In all these cases an atomic analogy prevails in the composition of the salts. The formation of *double*, or as they are sometimes called *triple salts*, is also a common occurrence: a familiar instance is afforded by the *tartrates of potassa and of soda*, the solutions of which, when mixed and evaporated, yield a crop of distinct double crystals; and *emetic tartar* is a double tartrate of antimony and potassa.

Crystallization is often accelerated by introducing into the solution a *nucleus*, or solid body. Thus we see *sugar-candy* crystallized upon strings, and *verdigris* upon sticks, and *sulphate of copper* upon wire baskets. Absorbent and rough surfaces are particularly favourable to these crystalline depositions: thus, if we tie two or three pieces of cotton, or woollen thread, upon a smooth glass rod, and immerse it into a solution of alum, nitre, or other easily crystallisable salt, the clusters of crystals will be confined to those particular spots. The annexed cut represents a glass rod upon which clusters of alum crystals have been thus deposited.



There are cases in which it is particularly advantageous to put a few crystals of the dissolved salt into the solution, which soon cause a crop of fresh crystals; and if, for this purpose, we select very perfect forms, they will increase in size as the evaporation proceeds, and being daily turned, so that all sides may receive increments of solid matter in succession, they often produce large crystals of great perfection; but, in proceeding thus, care must be taken not to elevate the temperature of the solution, for if it be raised only a few degrees, portions of the newly-formed crystals are generally re-dissolved. "Dr. Wollaston made a remark upon the spontaneous growth of large crystals at the expense of small ones in the same solution, exposed to changes of temperature, which illustrates in a beautiful manner, the alternate ascendancy of the two antagonist forces. When the temperature rose the solvent power of the liquid was increased, and some of the solid matter of the crystals was abstracted; but when the temperature again fell this was deposited in a greater proportion upon the larger masses than upon the smaller, so that the latter were in the end entirely taken up and deposited upon the former." (DANIELL, § 106.) In some instances, if there be two salts in solution, that will most readily separate of which the crystals have been introduced. Thus, if we dissolve two parts of nitre and three of sulphate of soda in five of warm water, and fill two bottles with the solution, putting into one a crystal of nitre, and into the other a crystal of sulphate of soda, and placing both in ice-cold water, nitre only will crystallize in the one, and sulphate of soda in the other.

Certain saline solutions excluded from the *air*, will frequently crystallize the instant that air is admitted. For this purpose a strong solution of sulphate of soda (3 lbs. of the crystallized salt, to 2 lbs. of water) may be most conveniently used: it should be poured whilst hot into a flask, and tied over with bladder, or secured by a good cork: when cold it remains liquid, but on perforating the bladder, or withdrawing the cork, it gradually shoots from the surface downwards, into a fibrous mass of crystals. This phenomenon has been referred to atmospheric pressure; but a film of olive-oil, or oil of turpentine poured upon the surface of the saline solution, equally prevents crystallization. On pouring out the liquid, or plunging a thermometer into it, it congeals; at the same time heat is evolved, and the bulk increased. (GAY LUSSAC, *Annales de*

Chimie, LXXXvii.) Graham (*Edinb. Phil. Trans.*, 1828,) ascribes it to the absorption of air by the water holding the salt in solution. In other cases, agitation, or the dropping in of a crystal or other solid, produces the same effect. Such phenomena have been shown by Ure (*Quart. Journ.*, vol. x.) to be affected by electrical changes; he found that, in the voltaic circuit, crystallization always began at the negative pole; but as alkali is there elicited, it may have tended to accelerate the process; or the acid evolved at the positive pole may have retarded it: or the relative volumes of gaseous products at the two poles may have interfered.

Vibration or friction sometimes curiously induces a crystalline precipitate; thus, if tartaric acid be added in excess to a solution of potassa so weak as not immediately to throw down the bitartrate, tapping the glass, and especially rubbing its interior with the end of a glass rod, will occasion a crystalline precipitate, and in the latter case the crystals will be deposited upon the lines which had been traced by the rod. A solution of a magnesian salt with carbonate of ammonia and phosphate of soda, adequately diluted, and similarly treated with a glass rod, exhibits the same phenomenon.

The presence of *light* also influences the process of crystallization. Thus we see the crystals collected in camphor-bottles in druggists' windows always most copious upon the surface exposed to light; and if we place a solution of nitre in a room which has the light admitted only through a small hole in the window shutter, crystals will form most abundantly upon the side of the basin exposed to the aperture through which the light enters, and often the whole mass of crystals will turn towards it. On looking over the preparations upon the shelves of the laboratory, we frequently meet with analogous cases of crops of crystals formed upon the sides of the bottles facing the windows.

Many saline solutions form arborescent crystalline pellicles, when left to spontaneous evaporation, which slowly travel up the sides of the basin, and gradually proceed down upon the outside; this process also often begins on the side nearest the light, and is sometimes confined to it. Acetate of lime exhibits this appearance in a very beautiful manner. (AIKIN'S *Dict.*, Art. LIGHT.) It is often the exclusive result of the capillary attraction of the crystals formed upon the edge of the solution.

The forms of crystals are sometimes modified by the *medium* from which they are deposited, independent of any chemical change: thus in foul and muddy liquids the crystals are usually deposited in their simplest forms; in gelatinous and saccharine solutions crystals are generally single, and remarkably sharp and regular. Common salt deposited from an aqueous solution containing urea, crystallizes in octohedra instead of cubes, which are its usual figure; and sal ammoniac under the same circumstances forms cubes, whereas in pure water its crystals are octohedral. Berzelius says, that very large crystals of nitre may be obtained from its solution in boiling lime-water, which has no analogous effect upon other salts.

Some substances remarkably interfere with the appearance and forms of crystals, although contained in them in very minute quantities; this is especially the case with some of the *hydrocarbons*. If 1 part of the liquid hydrocarbon obtained by the compression of oil-gas, be mixed with

8 or 10 parts of strong oil of vitriol, a dark liquor is produced; from this, when diluted with water, filtered, and converted by the addition of carbonate of potassa into a sulphate of potassa, a salt is obtained, which, upon crystallization, is nacreous, in the form of scales, and has nothing in its appearance common to sulphate of potassa: it is however that salt; and is thus affected by the presence of a substance which sometimes does not amount to a two-hundredth part of the salt. The same substance has a still greater power over the sulphate of copper, and in increased quantities (still comparatively small), influences the appearances of other saline bodies. (FARADAY.)

A curious and important fact in regard to crystallization, was first noticed by Mitscherlich, namely, the assumption by the same substance of two *incompatible* crystalline forms: such bodies are therefore called *dimorphous*. This is the case with *sulphur*, which when crystallized by fusion yields oblique rhombic prisms, but is deposited from certain of its solutions in rhombic octohedrons. Carbon, in the form of *diamond*, crystallizes in octohedrons, but as *graphite*, in hexagonal plates. Carbonate of lime in *calcspar* has the rhombohedral structure, but in *arragonite* that of the rectangular octohedron; and there are other analogous instances. It has been found in regard to these cases of dimorphism that each form has its peculiar density; the specific gravity of calcspar for instance being 2.71; that of arragonite is 2.94. The temperature too at which the crystals are formed is another influencing cause: thus when carbonate of lime is precipitated by adding chloride of calcium to carbonate of ammonia, the grains of the powder are rhombohedral if thrown down at the temperature of 50°, but octohedral, if at 150°. (G. ROSE, *Phil. Mag.*, xii. 465.)

There are, moreover, some cases in which solids themselves change their molecular arrangement: thus sugar which has been boiled down to such a consistency as to solidify on cooling, forms a transparent vitreous mass, as seen in what is termed *barley-sugar*; but this, if kept for some time, becomes opaque, granular, and friable. Old brass wire is apt to grow brittle, apparently in consequence of acquiring a crystalline texture not perceptible in its original state of ductility: and it is suspected that the friction, vibration, and changes of temperature to which the axles of railroad carriages are especially subject, may produce in these a similar change, and that although originally constructed of fibrous and tough wrought iron, they may from such causes acquire a crystalline and brittle structure. Prismatic crystals of *sulphate of nickel* and of *seleniate of zinc*, when exposed to the sun, become opaque, and break up into small octohedrons. Crystals of *sulphate of magnesia* or of *sulphate of zinc*, heated in oil to a temperature of about 126°, become opaque, and when broken are found to consist of a number of individual crystals, easily separated. (MITSCHERLICH. See also METHUON, *Quart. Journ.* i. 123, and GREGORY WATT *on the effect of slow cooling upon certain substances*, *Phil. Trans.*, 1804, 279.) Dr. Macculloch has noticed the crystalline texture occasionally acquired by some kinds of sandstone, which, having served for the hearths of furnaces, have been long exposed to heat, though always far below their point of fusion. But no modification of form is more remarkable than that of *glass*, a state, of which many bodies are susceptible, and characterized by a curved or conchoidal

(*glassy*) fracture; it never breaks with plane surfaces or *sparry*. Under certain circumstances, however, vitreous compounds pass into crystalline forms, and in large masses of glassy slag, globular nodules of radiating and acicular crystals are not very uncommon. *Arsenious acid* presents a similar phenomenon: when recently fused or sublimed it is usually glassy and transparent, but it gradually becomes an opaque, white, crystalline solid; the change commencing at the surface, and gradually proceeding to the centre. This change from the vitreous to the crystalline state sometimes takes place suddenly, and gives rise to a curious phenomenon observed by G. Rose: the vitreous acid, when dissolved in hot and dilute hydrochloric acid, deposits crystals of the opaque acid, and a flash of light is emitted at the formation of each crystal; this appearance is not observed when the hydrochloric solution is made with the opaque or crystalline, instead of the transparent or glassy, acid. According to Pelouze (*Ann. Ch. et Ph.*, 3 Ser. vii. 176,) substances are more easily decomposed when in the amorphous than in the crystalline form: he cites, binoxides of mercury and manganese, and carbonate of lime, as instances; but his conclusions are not admitted by Gay Lussac (*Ann. Ch. et Ph.*, 3 Ser. vii. 113).

There are other cases in which what has been termed a species of dimorphism is evidently produced by changes of temperature. Thus the red sulphuret and the red oxide of mercury both become black when highly heated, but reassume their red colour on cooling; periodide of mercury is often yellow whilst hot, but becomes scarlet as it cools. (WARINGTON, *Trans. Chem. Soc.*, I.) Oxide of zinc is yellow whilst hot, and white when cold. Even gaseous bodies are susceptible of changes of this kind, of which nitrous acid vapour furnishes an instance, being nearly colourless when very cold, but of a deep orange when heated. When precipitated sulphuret of antimony is dried at about 400° it retains its deep orange colour, but when heated a little higher, it shrinks, blackens, and acquires a metallic lustre, without further loss of weight; and on the other hand, the black sulphuret, when strongly heated, and suddenly cooled by throwing it into water, acquires a brown colour.

Certain metallic oxides, such as alumina, peroxide of tin, and oxide of chromium, become insoluble in acids after having been heated to redness; and some of them, in passing from the soluble to the insoluble state, suddenly become luminous, and rise greatly in temperature; this is remarkably the case with Gadolinite, which glows when heated, and changes colour, but sustains no change of weight.

The cause of many of these extraordinary phenomena, in which bodies undergo changes in form and properties, whilst their composition is not apparently altered, may in some instances no doubt be referred to modifications of their molecular arrangements; in other cases the loss or evolution of heat is apparent. "The circumstance," says Professor Graham (*Elem. Ch.*), "most certain respecting this change in bodies is that they do not contain a quantity of heat after the change, which they must have possessed before its occurrence, in a combined or latent form. No ponderable constituent is lost, but there is this loss of heat. A change of the arrangement of the particles, it is true, might occur at the same time in some of these bodies, such as is observed when sulphite of soda is converted by heat into a mixture of sulphate of soda

and sulphuret of sodium, without change of weight; but it would be difficult to apply an explanation of this nature to oxides, such as alumina and peroxide of tin, which contain only two constituents. The loss of heat observed will afford all the explanation necessary, if heat be admitted as a constituent of bodies equally essential as their ponderable elements. As the oxide of chromium possesses more combined heat when in the soluble than in the insoluble state, the first may be justly viewed as the higher *caloruret*, and the body in question may have different proportions of this as well as of any other constituent."

Independent of the beautiful application of the process of crystallization in refined chemistry to determine the *nature* of bodies by the careful inspection of their forms, the manufacturer avails himself of it to cleanse, purify, and prepare a number of substances useful in the arts, the purity of which is often judged of by the regularity and perfection of their crystalline figures. Common salt is thus obtained by the evaporation of sea-water, and of brine-springs, in consequence of its tendency to crystallize in hot liquors, which retain the other salts that are present in more permanent solution. Epsom salt, or sulphate of magnesia, is freed by crystallization, from the chloride of magnesium with which it is mixed in the residue of sea-water, after its common salt has been taken out: the magnesian chloride is very difficultly crystallizable, and remains in what is called the *mother liquor*, or residuary solution, which on account of its excessive bitter taste, is known in our salt-works by the name of *bittern*. Nitre is refined, by the facility of its crystallization, for the manufacture of gunpowder, and so cleansed of common salt and other impurities with which it is usually contaminated in the state in which it is imported from India. Numerous other instances of the application of the process of crystallization to the purposes of the arts and manufactures will appear in the sequel.

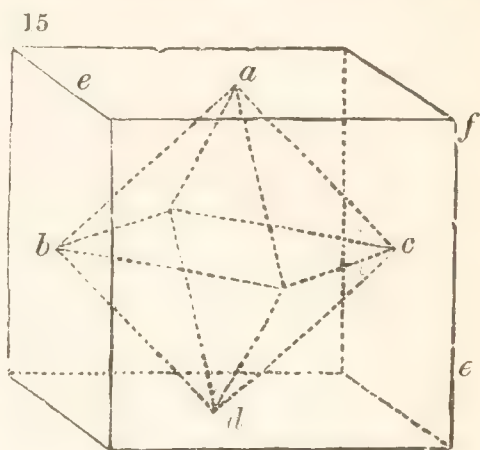
§ 2. THEORIES OF CRYSTALLIZATION.

WE may now proceed to notice the *structure* of crystallized bodies, upon which the *Theories of Crystallization* are founded.

It has already been observed, that crystallized bodies, natural and artificial, affect one form in preference to others. The fluor-spar of Derbyshire crystallizes in cubes; so does common salt. Nitre assumes the form of a six-sided prism, and sulphate of magnesia that of a four-sided prism. But these forms, especially as respects natural crystals, are liable to various modifications. Fluor-spar sometimes crystallizes in the form of octohedra; and there are so many forms of carbonate of lime that it is difficult to select that which most commonly occurs. Romé de L'isle referred these variations of form to certain truncations of an invariable primitive nucleus; and Gahn afterwards observed, that when a piece of calcareous spar was carefully broken, all its particles were of a rhomboidal figure. This induced Bergman to suspect the existence of a primitive nucleus in all crystallized bodies. (*Phys. and Chem. Essays*, II. 1.) When Haüy entered this field of inquiry, he not only corroborated the opinions of Bergman, and submitted former hypotheses to experimental proof, but traced with much success the laws of crystallization, and pointed out the modes of transition from primary to secondary figures. (*Traité de Minéralogie*, Paris, 1801.) Since the time of Haüy

the study of crystallization, especially in its relations to mineralogy, has been pursued and extended by G. Rose, (*Elements of Crystallography*,) by Professor Whewell, (*Phil. Trans.*, 1825,) by M. Mohs, and by Professor Weiss, of Berlin; the latter is the founder of a new system of crystallography, having reference to the geometrical relations of their exterior forms rather than to their ultimate molecules or internal structure.

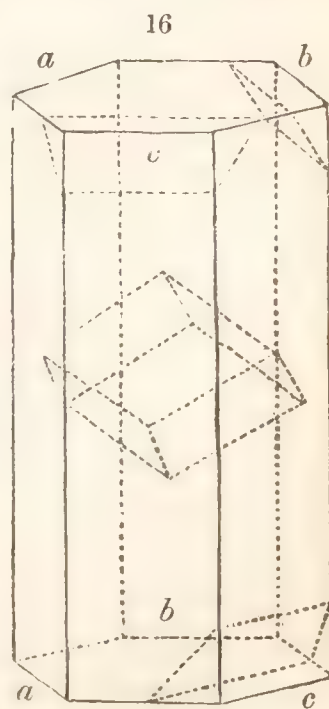
Those who are in the habit of cutting and polishing certain gems, have long known that they only afford smooth surfaces when broken in one direction; and that in others the fracture is irregular and uneven. This is the case with crystallized bodies in general. If we attempt to split a cube of fluor-spar with the blade of a knife, assisted by a hammer, we shall find that it will only yield kindly in the direction of the solid angles; and pursuing the division in these directions, an octohedron will be the resulting figure, as in fig. 15. The new planes resulting from this 'cleavage' of the crystal, are called its *cleavage-planes*. The line produced by the meeting of two planes is the *edge* of the crystal; and the meeting of any two lines or edges, forms a *plane angle*. A *solid angle* is produced by the meeting of three or more plane angles. In the annexed diagram, *a b c d* are the exterior planes of the crystal; *e e* its edges; *f f* its solid angles. (For further details respecting these terms, see BROOKE'S *Familiar Introduction to Crystallography*.)



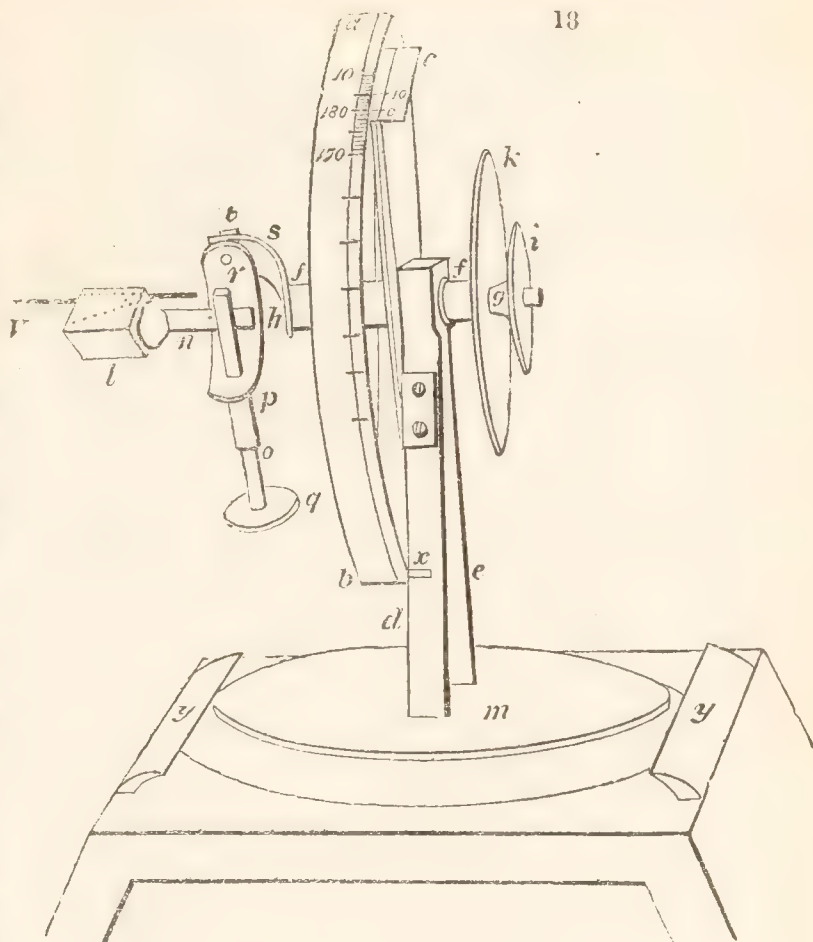
In splitting a six-sided crystal of calcareous spar, we find that of the six edges of the superior base three alternate edges only will yield to the blow: those, for instance, marked *a, b, c*, (fig. 16); and the division will take place in a plane inclined at an angle of 45° . The three intermediate edges resist this division. But in dissecting the inferior base of the crystal, the intermediate edges will alone yield, namely, *a, b, c*. If we continue this dissection in the same directions, we shall at length obtain the obtuse rhomboid, which is seen in this diagram in its relative situation to the including prism.

We thus then arrive at the *primitive form* of the calcareous spar; and from whatever secondary form it has been obtained, it is always a *rhomboid*, having obtuse angles of $105^\circ 5'$. But an obtuse rhomboid is also the primitive form of other bodies, as of pearl-spar, iron-spar, and tourmalin. But here the inclination of the surface points out a difference. Thus the primitive angle of pearl-spar is $106^\circ 5'$, of iron-spar 107° , (WOLLASTON, *Phil. Trans.*, 1812,) and of tourmalin $113^\circ 10'$.

The *temperature*, however, at which these measurements are taken, should be noted, for it affects the mutual inclinations of the planes of certain crystals. In the case of carbonate of lime, it amounts, according to Mitscherlich (*Ann. Ch. et Ph.*, xxv. 108), to as much as $8'5$, in the interval of temperature between 32° and 212° . As the temperature augments,



duated only in part in the annexed sketch). *c* is a brass plate, screwed upon, and supported by, the pillar *d*, and graduated as a vernier. *ff* is the axle of the circle *a b*, and passes through the upper part of the two pillars *d e*, the other ends of which are inserted into a wooden base *m*. *g h* is an axle, enclosed within *ff*, and turned by means of the smallest circle *i*, which communicates a motion to all the apparatus on the left of *h*, without moving the principal circle *a b*. *k* is a circle, to which is attached the axle of the principal circle. If therefore we would move the latter, it will be done by moving *k*, and as the axle of the principal circle includes that of the apparatus on the left of *h*, we must necessarily give a motion to the whole instrument by moving the circle *k*.



These two movements being understood, let us now suppose that we want to measure a crystal; a rhomboid of carbonate of lime, for instance*. Let *l* be the rhomboid, attached by means of wax to one end of a plate of brass *n*; the other end of the plate being placed in a slit in the upper part of the circular brass stem *o*, which passes through the tube *p*, to which it is so adjusted as to allow of being moved either up or down, or circularly, by means of the circle *q*. The tube *p* is fixed to the curved brass plate *r*, which is attached, but so as to allow of motion, to another curved plate *s*, by means of a pin *t*, the other end of the latter plate being connected with the concealed axle *g h*, to which a motion is given by turning the little circle *i*. By means of the pin *t* and the tube *p*, therefore, we have two motions, in addition to the two before described as belonging to the axles of the instrument. The inner axle, however, may be said to be the centre of all the motions. It will, therefore, be of advantage that the rhomboid of carbonate of lime should be placed as nearly on a line with that axle as possible: this will be sufficiently adjusted by means of the stem *o*, which admits of being raised or depressed at pleasure.

The use of this instrument depends on the reflecting power of the polish on the natural planes, or fractured surfaces of minerals: and that this is in some cases very powerful, any one may convince himself by looking upon a brilliant plane, held beneath the eye, with its edge nearly

* As it is necessary that this instrument when used should be perfectly steady, it should be placed upon a firm table, and may be raised to a convenient level (about

a foot above it), by its case, the top of which is represented in the wood-cut; *m* is the base of the goniometer, and *y y*, two hollowed slips of wood which receive it.

touching the lower lid, and not far distant from a window; he will then observe the reflection of the bars very distinctly. Let us then suppose the goniometer, as above represented, to be distant from a window from eight to twenty feet. Let, then, v be a *black line* (the use of this is essential) drawn on the wainscot between the window and the floor, and *perfectly parallel* with the horizontal bars of the window. If, then, the eye be placed almost close to the rhomboid l , a reflection of one of the bars will be seen on one of its planes. Let us suppose the reflection to be in the direction of the lower dotted line on the plane; and it will be clear that it cannot be parallel with the bar of the window, not being even with the black line v . It must therefore be adjusted. This may, perhaps, be done by slightly drawing to the left the circle q , which communicates motion by means of the pin t ; or perhaps it may be done by giving a circular motion to the stem o . By one of these two motions, or by both, it may certainly be effected. If, however, the reflection appears to be like the upper dotted line, that is, parallel with the black line, v , we must first convince ourselves that it is so, simply by depressing the crystal a little by means of moving the little circle i , so as to bring the reflection *upon the black line*. This being adjusted, which must be done precisely, we then turn the crystal, by turning the little circle i , until the reflection of the *same bar* be seen on the next plane, perfectly *on a line with and upon the black line v* . However, in adjusting the second, we may disturb the first reflection. By perseverance it will be found that both can be adjusted by means of one or other of the movements by the stem o , or the pin t , or by the help of both, and a short experience will do away the chief difficulties. Both reflections being precise, we are now, by means of the circle k , to turn the principal circle until it is arrested by the stop x on the pillar d ; it will then be found that 180 on the principal circle coincides with 0 on the vernier. In doing this however, we may slightly disarrange the reflections on the plane of the crystal, which may be re-adjusted simply by moving the little circle i , which will not disturb the principal circle $a b$: we must be certain, however, *that 180 on it forms a line with 0 on the vernier, at the same time that the reflection of the bar is seen along the black line*. One movement more, and the measurement will have been made. Turn the circle k , keeping the eye almost close to the rhomboid, until the reflection of the *same bar* is seen on the adjoining plane *precisely upon the black line v* , and the operation is completed. It must then be observed what proportion of the principal circle has been moved. Suppose that 105 on it be now on a line with 0 on the vernier;—it is the value of the angle. But suppose it to be a little more than 105 and less than $105\frac{1}{2}$: it must then be observed *which line of the vernier touches, or forms but one line with*, another line on the principal circle: suppose it to be 5 on the vernier, the angle is then $105^{\circ} 5'$, which is the true value of the obtuse angle of a rhomboid of carbonate of lime.

In pursuing the method of dissection above described, Häüy obtained certain *primitive forms*; namely, the parallelopipedon, including the cube, &c. (fig. 19); the tetrahedron (fig. 20); the triangular prism (fig. 21); the octohedron (fig. 22); the hexahedral prisim (fig. 23); the rhomboidal dodecahedron (fig. 24); the triangular dodecahedron (fig. 25). From these he deduced the *secondary forms*, which he assumed as arising from

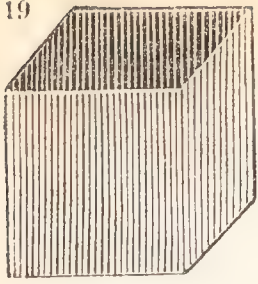
decrements of particles taking place on different edges and angles of the primitive forms. Thus a cube, having a series of decreasing layers of cubic particles upon each of its six faces, will become a dodecahedron, if the decrement be upon the *edges* (fig. 26); but an octohedron, if upon the *angles*; and by irregular, intermediate, and mixed decrements (fig. 27), an infinite variety of secondary forms would ensue, as the annexed figures show. Upon this hypothesis, therefore, every crystal is supposed to include an invariable nucleus, or *primitive form*, from which the *secondary forms* are derived, by certain *laws of decrement**.

These illustrations have been taken from Haüy as furnishing the simplest instances of his theoretical views, but other crystallographers have given very different statements of the number and nature of the primary forms. Brooke (*Introduction*, p. 6) has enumerated fifteen, namely, 1. The *cube*, contained within six square planes (fig. 19). 2. The *regular tetrahedron*, contained within four equilateral triangular planes (fig. 20). 3. The *regular octohedron*, resembling two four-sided pyramids united base to base; the planes are equilateral triangles, and the common base of the two pyramids (or the *base of the octohedron*) is a square (fig. 22). 4. The *rhombic dodecahedron* contained between twelve equal rhombic planes (fig. 24). 5. The *octohedron with a square base* (fig. 28), contained within eight equal isosceles triangular planes; the square base distinguishes it from figures 29 and 30, and is the only part of the figure which is constant. 6. The *octohedron with a rectangular base*; its planes are generally isosceles triangles, *but not equal* (fig. 27). 7. The *octohedron with a rhombic base*, contained within eight equal *scalene* triangular planes: all its dimensions are variable (fig. 30). 8. The *right square prism* (fig. 31). (A prism is a solid whose lateral edges are parallel, and whose terminal planes are also parallel: those which stand perpendicularly when resting on their base, are called *right prisms*; those which incline, are called *oblique prisms*.) 9. The *right rectangular prism* (fig. 32), whose three edges, *a b c*, are unequal; for if any two of these were equal, the prism would be square. 10. The *right rhombic prism* (fig. 33), differing from the preceding in the planes *a a* being rhombs. 11. The *right rhomboidal prism* (fig. 34), in which the planes *a a* are rhomboids. 12. The *oblique rhombic prism* (fig. 35). 13. The *oblique rhomboidal prism* or *doubly oblique prism* (fig. 36). 14. The *rhomboid*, or *rhombohedron*, bounded by six equal rhombic planes (fig. 37). 15. The *regular hexagonal prism* (fig. 38). In reference to the geometrical relations of these forms to each other, and to the production of secondary forms, I must again refer to Brooke's *Introduction*.

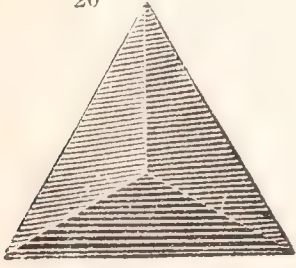
* "This," says L. Gmelin, "is only a theoretical expression, which is applied by the author to the calculation of the formation of the secondary surfaces, and leads to the assumption that crystals in their first origin have the same form which they possess when they have attained their perfect

state. But, according to the views of Weiss, the angles of the different primitive and secondary surfaces may be simply deduced from the mere relations of the linear dimensions of a crystal, without the assumption of so unnatural an hypothesis as that adopted by Haüy."

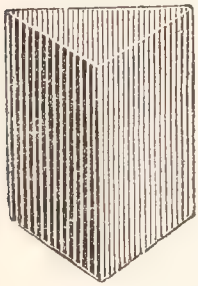
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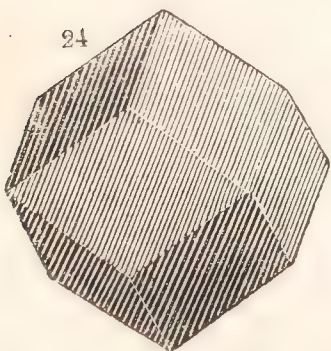
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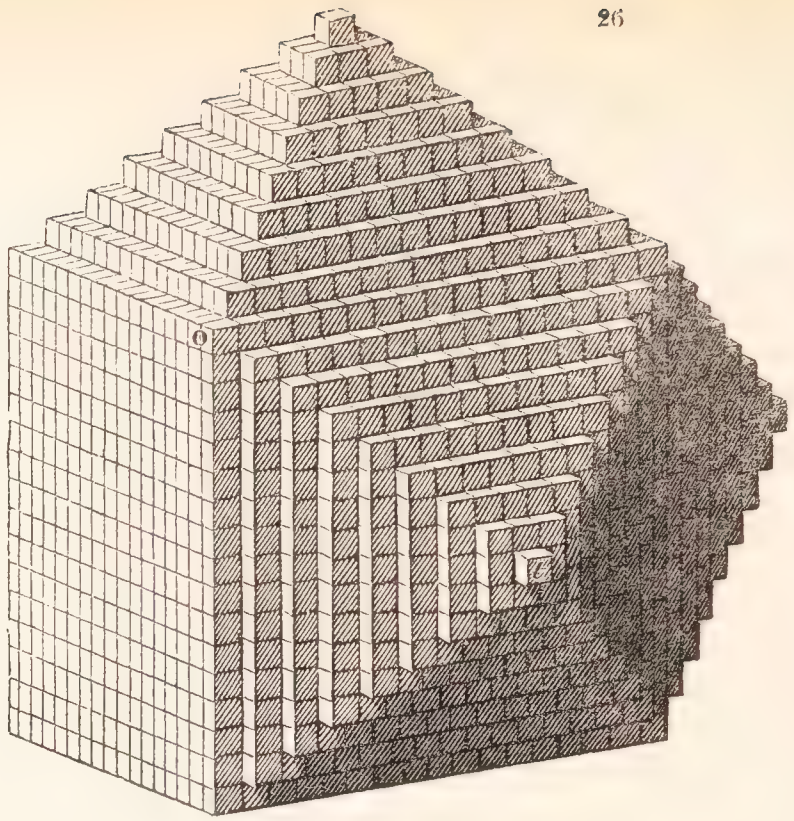
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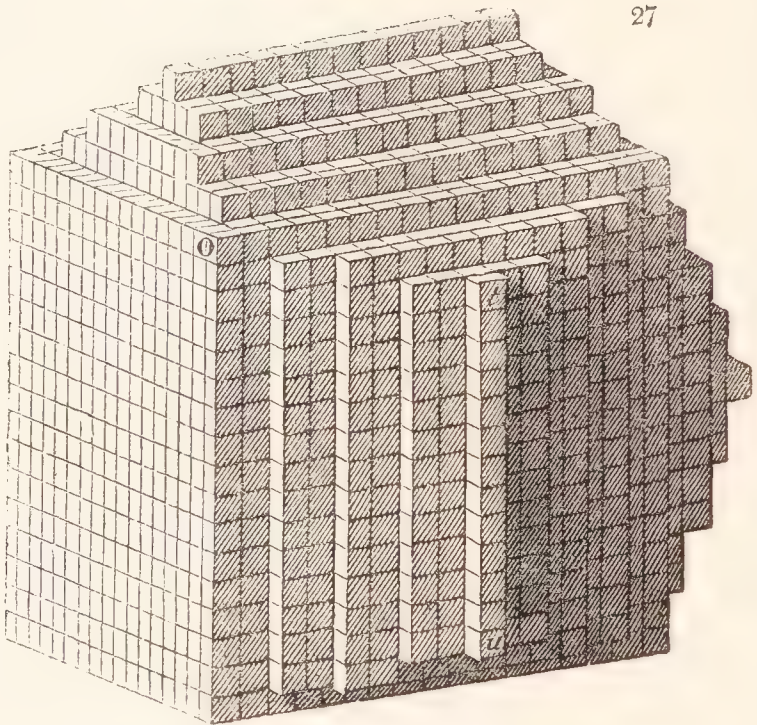
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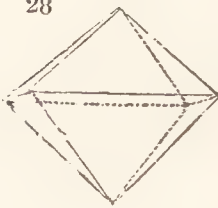
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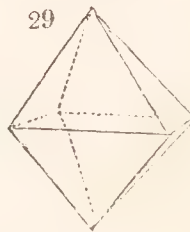
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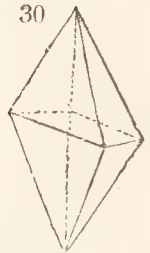
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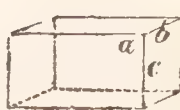
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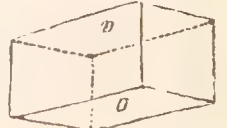
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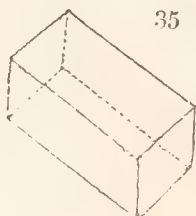
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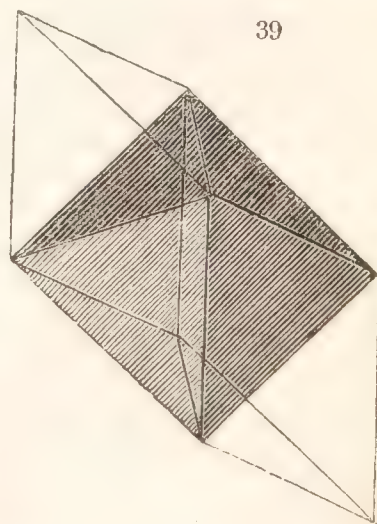


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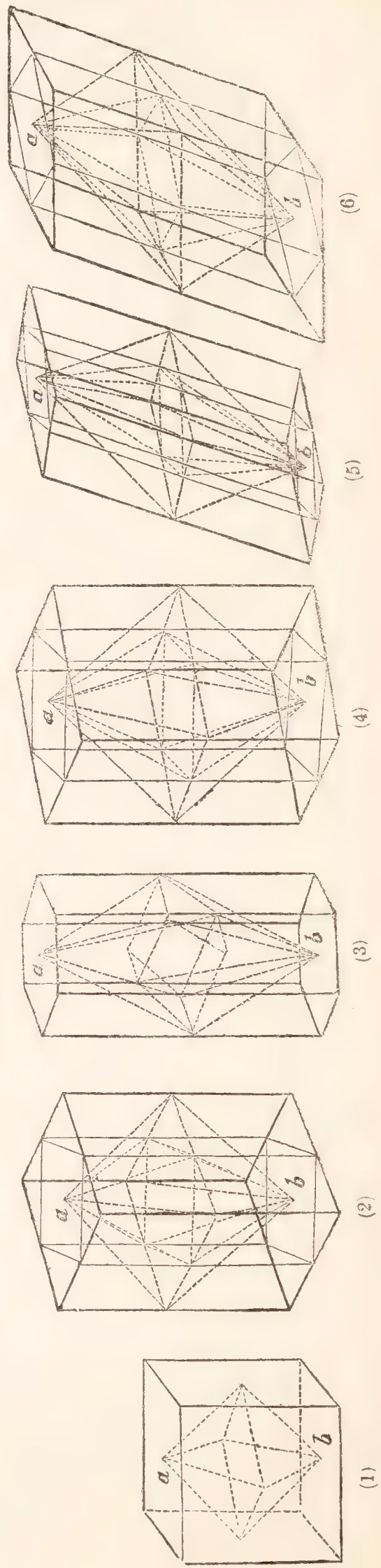
The geometrical forms of crystals have been referred by Weiss and Mohs to certain lines, in respect to which each face is accompanied by others having the same positions and properties, and which are termed *axes of symmetry*. A rhomboid of calc-spar, for instance, may be so placed with one of its obtuse angles uppermost, as that the three faces which meet there shall be equally inclined to the perpendicular line: "In this position every *derivative* face which is obtained by any modification of the faces or edges of the rhombohedron, implies either three or six such derivative faces; for no one of the three upper faces of the rhombohedron has any character or property different from the other two; and therefore there is no reason for the existence of a derivative from one of the primitive faces which does not equally hold for the others. Hence the derivative forms will in all cases contain none but faces connected by this kind of correspondence; the axis thus made vertical will be an axis of symmetry, and the crystal will consist of three divisions ranged round this axis and exactly resembling each other. But this is only one of the kinds of symmetry which crystalline forms may assume: instead of being *uniaxal*, they may have three axes of complete and equal symmetry at right angles to each other, as the cube and regular octohedron; or two axes of equal symmetry perpendicular to each other, and to a third axis which is not affected with the same symmetry with which they are; such a figure is a square pyramid: or they may have three rectangular axes all of unequal symmetry, the modifications referring to each axis separately from the other two, such as a right rectangular prism. The law of crystalline symmetry is such, that if a face of a crystal be observed to bear a certain relation to one of the axes, other faces must fulfil the same condition with regard to the equal axes: hence it follows that the forms which are allied to the cube or octohedron, all of whose axes are equal, are few, simple, and of perfect symmetry." The table on the next page represents the six systems of Weiss, with their allied forms and their relations to heat and light. (DANIELL, §§ 124, 125; TURNER, *Elem. Ch.*)

As regards the molecular structure of crystals, we occasionally meet with cases to which the above theories of primary and secondary forms are not satisfactorily applicable. A slice of fluor-spar, for instance, obtained by making two successive and parallel sections, may be divided into acute *rhomboids*; but these are not the primitive form of the spar, because, by the removal of a tetrahedron from each extremity of the rhomboid, an *octohedron* is obtained (fig. 39). Thus, as the whole mass of fluor may be divided into tetrahedra and octohedra, it becomes a question which of these forms is to be called primitive, especially as neither of them can fill space without leaving vacuities, nor can they produce any arrangement sufficiently stable to form the basis of a permanent crystal. Mr. Daniell, in the following figures, has represented these constructions of the tetrahedron and octohedron each with tetrahedral and octohedral particles, in which it is seen that the tetrahedral structure is interspersed with octohedral vacuities, and the octohedral with tetrahedral spaces; so that one might be conceived to be taken out of the other. "All bodies," he

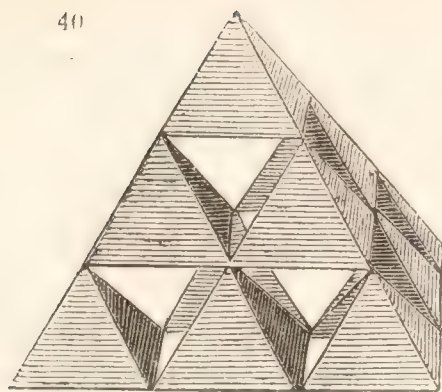


Systems of Crystallization.

PHYSICAL CHARACTERS.	SYSTEMS.	ALLIED FORMS.	EXAMPLES.
1 Single Refraction Expansion equal in all directions.	1 CUBIC, OCTOEDRAL, TESSULAR or REGULAR. 3 rectangular axes, all equal.	1 Cube. 2 Regular Octohedron. 3 Tetrahedron. 4 Rhombic Dodecahedron. 5 Trapezohedron.	Copper, Nickel, Gold, Alum, Common Salt, Arsenious Acid, Fluor Spar, and Iron Pyrites.
2 Double Refraction. Expansion not equal in all directions.	2 RIGHT SQUARE PRISMATIC. 3 rectangular axes, 2 equal	6 Square Prism. 7 Octoedron with a square base.	Idocrase, Anatase, Ferrocyanide of Potassium, and Bicyanide of Mercury.
	3 RHOMBOHEDRIC. 3 equal axes, not rectangular; 1 perpendicular to the three.	8 Rhombohedron. 9 Bipyramidal Dodecahedron. 10 Hexangular Prism.	Calcareous Spar, Nitrate of Soda, Ice, Tourmaline, Quartz, and Amethyst.
	4 RIGHT, RECTANGULAR or RHOMBIC PRISMATIC. 3 rectangular axes, no two equal.	11 Right Rectangular Prism. 12 Rhombic Ditto. 13 Rectangular Octohedron. 14 Rhombic Ditto.	Sulphate of Potash, Nitre, Rochelle Salt, Topaz, Arragonite, Bichromate of Potash, Citric Acid, Sulphate of Magnesia, and Sulphate of Zinc.
	5 OBLIQUE, RECTANGULAR or RHOMBIC PRISMATIC. 2 axes oblique, the third perpendicular to both.	15 Oblique Rectangular Prism. 16 Rhombic Ditto. 17 Rectangular Octohedron. 18 Rhombic Ditto.	Feld Spar, Epidote, Carbonate of Soda, Glauber Salt, Sulphate of Iron, Chlorate of Potash, Borax, Sugar, Selenite, Acetate of Zinc, and Oxalic Acid.
	6 DOUBLY-OBLIQUE, PRISMATIC. 3 axes, all intersecting each other obliquely.	19 Doubly-oblique Prism. 20 Octohedron.	Axinite, Sulphate of Copper, Sulphate of Cinchonina, and Nitrate of Bismuth.

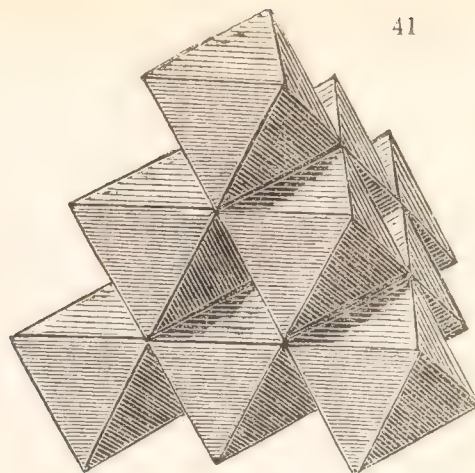


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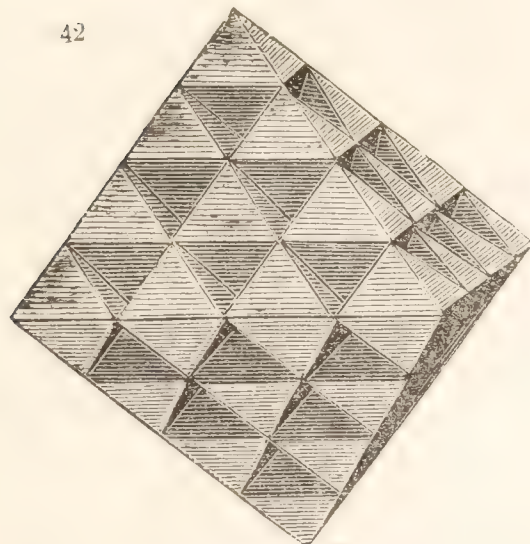
Tetrahedral Tetrahedron.

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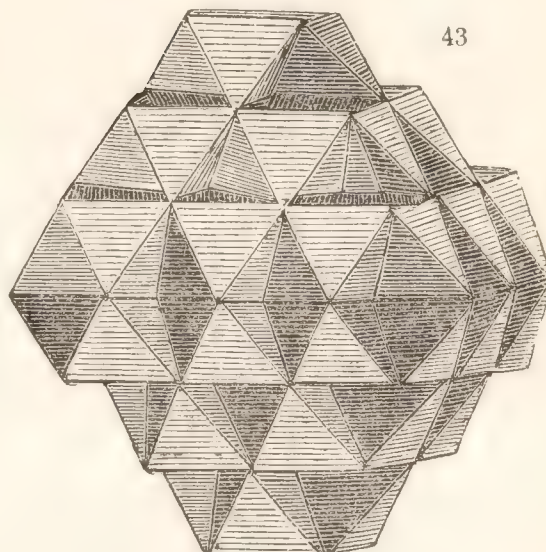
Octohedral Tetrahedron.

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Octohedral Octohedron.

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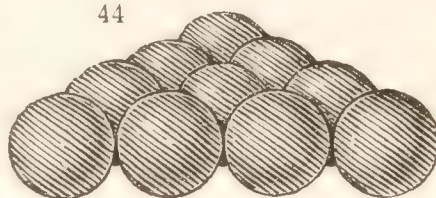


Tetrahedral Octohedron.

observes, "may be considered as attracting each other, as if the whole of their matter were condensed into their centres of gravity, which therefore would in all cases be drawn as closely as possible together: under this law solid tetrahedra and octohedra would apply themselves to each other by their sides, and not by their edges."

To obviate such incongruities, Dr. Wollaston (*Phil. Trans.*, 1813), following out an hypothesis previously suggested by Dr. Hooke, proposed to consider the primitive particles as *spheres*, which, by mutual attraction, have assumed that arrangement which brings them as near as possible to each other. When a number of similar balls are pressed together in the same plane, they form equilateral triangles with each other (fig. 44); and if balls so placed were cemented together and afterwards broken asunder, the straight lines in which they would be disposed to separate would form angles of 60° with each other. A single ball, placed anywhere on this stratum, would touch three of the lower balls, and the planes touching their surfaces would then include

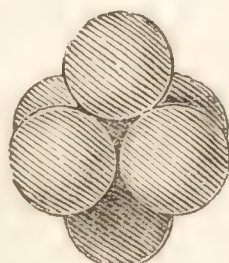
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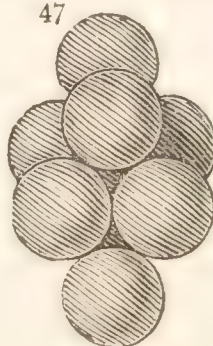
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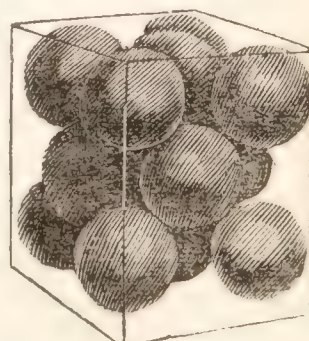
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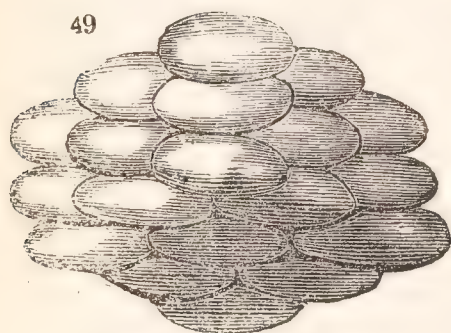
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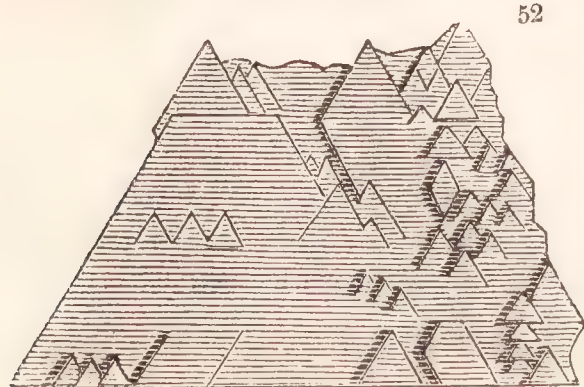
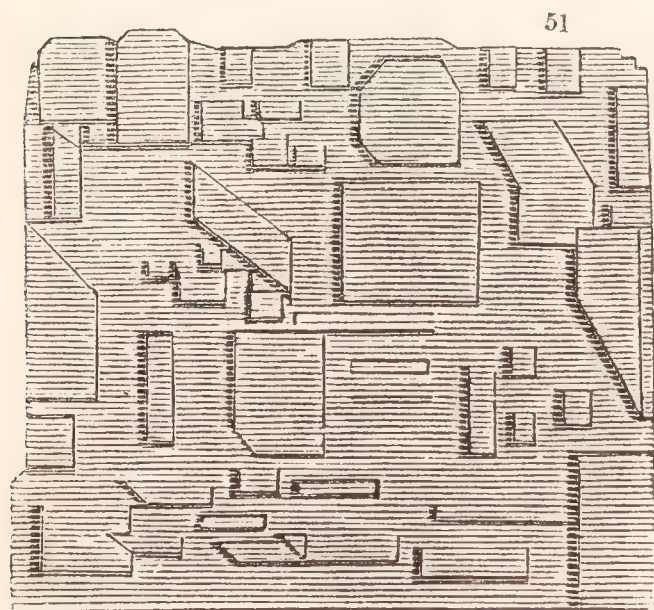


a regular tetrahedron (fig. 45). A square of four balls, with a single ball resting upon the centre of each surface, would form an octohedron (fig. 46); and upon applying two other balls at opposite sides of this octohedron, the group will represent the acute rhombohedron (fig. 47); or by placing a ball on each face of the octohedron, it becomes a cube (fig. 48). Thus the difficulty of the primitive form of fluor, above alluded to, is done away, by assuming a sphere as the ultimate molecule. By oblate and oblong spheroids other forms may be obtained. Thus by



oblate spheroids having their axes in the proportion of 1 to 2.87, an oblate rhomboëdron, the angles of which would correspond with those of calc-spar, would result, and all such solids would split in directions parallel to their faces (fig. 49). With *oblong* spheroids, on the contrary (fig. 50), the centres would approach nearest to each other by mutual attraction when

their axes were parallel and their shortest diameters in the same plane; whence a solid which would split into plates at right angles to its axis, and the plates would be divisible into equiangular three or six-sided prisms; a cleavage belonging to phosphate of lime, to the beryl, and other minerals.



Daniell (*Quarterly Journal of Science and the Arts*, vol. i., and *Journal of the Royal Institution*, vol. ii.) has suggested some curious confirmations of Wollaston's hypothesis. It has already been stated that if an amorphous piece of alum be immersed in water, and left quietly to dissolve, it is unequally acted upon by the fluid (see fig. 1, p. 5): and the mass presents the forms of octohedra, and sections of octohedra, as it were carved or stamped upon its surface. This appearance (more definitely represented in figs. 51 and 52) is produced when the attraction of the water for the solid is nearly counterbalanced by its mechanical texture. The crystals formed by this species of dissection are highly curious, from their modifications and relative

positions, as the same group presents the primitive form, as well as its truncations and decrements.

Other salts yield other figures, and by more complicated chemical action, as of acids upon carbonate of lime, the metals, &c., analogous results are obtained. Here, then, instead of dividing a crystal by mechanical force, its structure is gradually developed by the process of solution. In these cases two circumstances are particularly remarkable;

the crystals are different; and their forms vary with the different faces of the original mass. In one direction we observe octohedra and sections of octohedra; in another, parallelograms, modified by certain determinate intersections. If, in either of these positions, we turn the mass upon its axis, the same figures are perceived at every quadrant of a circle; and if we suppose the planes continued, they will mutually intersect each other, and various geometrical solids will be constructed. In this way, alum alone furnishes octohedrons, tetrahedrons, cubes, four and eight-sided prisms, either with plain or pyramidal terminations, and rhombic parallelopipedons. It is evident, then, that no theory of crystallization can be admitted, which is not founded upon such a disposition of constituent particles, as may furnish all these modifications, by mere abstraction of certain individuals from the congeries, without altering the original relative position of those which remain; and these conditions may be fulfilled by such an arrangement of spherical particles, as would arise from the combination of an indefinite number of spheres endued with mutual attraction; and no other geometrical solid is adequate to the purpose; and where bodies afford crystals differing from the octohedral series, an analogous explanation is furnished by supposing their constituent particles to consist of oblate spheroids whose axes bear different proportions to each other in different substances. Hence we may also conclude, that the internal structure of all crystals of the same body is alike, however the external shapes differ. In corroboration of this hypothesis, Daniell remarks that the hexahedron is, of all geometrical figures, that which includes the greatest capacity under the least surface. "If, therefore, the ultimate particles of crystalline bodies be spheres or spheroids, the greatest possible number in the least space will be included in this form. It is probable that the exterior shape of every crystal is determined by the nucleus first formed by a certain definite number of particles, which, by the power of mutual attraction, overcome the resistance of the medium in which they were suspended, or from which they were separated. This number may vary with the solvent, or other contingent circumstances. Four spherical particles, thus united, would balance each other in a tetrahedral group, six in an octohedral group, and each would present particular points of attraction to which all subsequent deposits would be directed. Now, let us imagine two nuclei formed in the same solution, whose axes run in contrary directions; their increase will consequently be in contrary directions, and each will attract a particular system of particles from the surrounding medium. If these two systems should cross each other in their course, a greater number will be brought within the sphere of mutual reaction at the point of junction, and they ought to arrange themselves in the least possible compass. The facts here answer to the theory. If we select any crystals, having others crossing them nearly at right angles, and separate them, the points of junction invariably present an hexahedral arrangement."

We have already adverted to the important applications of the phenomena and process of crystallization to theoretical and practical chemistry. To the mineralogist, the science of crystallography is equally indispensable; it enables him to determine the species to which minerals belong, and to recognise their varieties by their external and mechanical characters.

CHAPTER II.

HEAT, LIGHT, AND RADIANT MATTER.

HEAT—ITS EFFECTS AND SOURCES.

HEAT may be considered as the antagonist power to attraction*, one of its most obvious effects being the dilatation or expansion of bodies; so that, whenever a body is heated, it is enlarged in bulk, and consequently diminished in density. These changes are temporary only; for, on cooling, the body regains its former dimensions, and a further reduction of heat causes a proportionate diminution of bulk; hence, bodies are said to *expand when heated*, and to *contract when cooled*; a law to which the exceptions are very limited.

We know nothing of the *cause* of heat, but we generally refer the effects perceived to the presence of a highly attenuated and imponderable fluid, the particles of which are presumed to repel each other, but to be attracted by all other substances: it is supposed to pervade all matter, and to be diffused over the universe. To this subtile matter the French nomenclaturists gave the name of *caloric*—a term which has been much employed, under the idea that the word *heat*, which is applied both to cause and effect, might lead to ambiguity: this, however, it need not; and whatever may be the cause of the phenomena, *the word heat may be used to denote that state or condition of a body which excites in us the sensation of heat.*

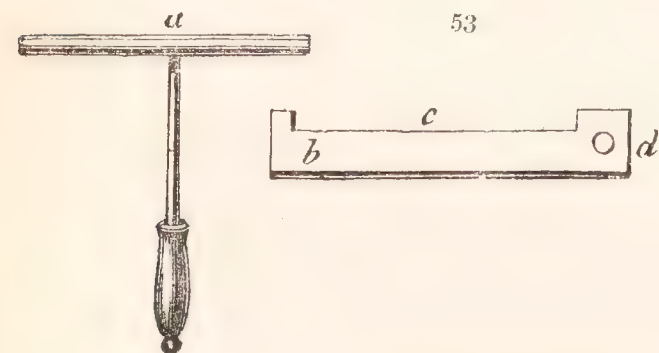
§ 1. EXPANSION IN GENERAL.

BODIES exist in nature under three forms,—*solids*, *liquids*, and *gases* or *vapors*; these three forms of matter suffer expansion and contraction in very different degrees, when exposed to similar changes of temperature; in *solids*, the change of dimensions is comparatively small, and refined means are necessary to determine and measure it; in *liquids* it is less opposed by cohesion, and therefore more obvious; and in *aëriform* bodies or *gases*, the particles of which are already mutually repulsive, it is extremely apparent: 1000 cubic inches of air, by being heated from the freezing to the boiling-point of water, sustain an increase in bulk of 375 parts; of water 45; and of iron only 4.

To show the *expansion of a solid*, a bar of metal for instance, we may be provided with a gauge which measures its length and breadth at ordi-

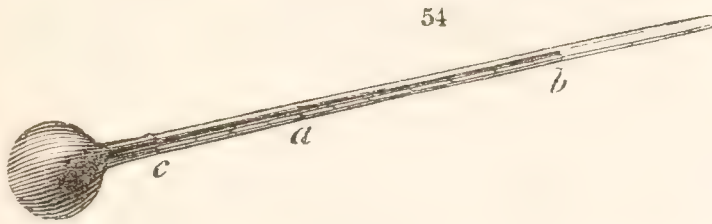
nary temperatures; and it will be found that, when heated, it will no longer pass through the apertures which readily admitted it when cold. *a* (fig. 53) is a brass bar with a handle attached, the length of which, at *common temperatures*, is exactly equal to the notch *c* in the plate *b*, and it

exactly passes into the circular aperture *d*. If the bar be now heated by plunging it into boiling water, it will be found so much enlarged in all its dimensions, as not to pass through the apertures. If, on the contrary, it be cooled by ice, it will then contract, and pass them more readily.



* Fresnel observes that a sensible repulsive power is conferred by heat upon bodies delicately suspended in vacuo.—(*Ann. Ch. et Ph.*, xxix., 57 and 107.)

The expansion and contraction of a *liquid*, when heated, are easily shown as follows: pour into a large thermometer tube (fig. 54) a quantity of brandy or other spirit, so as to fill the bulb, and rise in the stem up to the mark *a*. Plunge it into warm water, and the liquid will dilate and rise in the tube up to the point *b*; remove it, and suffer it to regain its original temperature, and its bulk will return to *a*; but if it now be put into ice, the liquid will contract, falling in the tube to *c*; but again expanding, when removed into the atmosphere at ordinary temperatures.



Aëriform bodies far exceed the former in expansibility. Place a thermometer-tube, with its open end in a glass of water, as in fig. 55, and apply the heat of the hand to the bulb *a*; this will be sufficient to expand the air within, so that bubbles will escape through the water, and on removing the source of heat, the water will mount in the tube, showing, by the place it occupies, the degree of expansion which the air had suffered.

Thus far the general fact of the *expansion of the different forms of matter by heat, and their contraction by cold*, is easily demonstrated; but there are peculiarities belonging to each, and applications resulting from them, which must be entered into more in detail.

§ 2. OF THE EXPANSION OF SOLIDS.

DIFFERENT solids possess different degrees of expansibility, and among them the *metals are most susceptible of change of bulk*; but each solid possesses a rate of expansion of its own. Lead, for instance, when heated from the freezing to the boiling point of water, expands in volume one-350th; iron, one-800th; glass, one-1000th; in other words, 350 cubic inches of lead become 351; 800 of iron, 801; and 1000 of glass, 1001. In consequence of the numerous purposes to which glass and the metals are applied, and with which these changes of bulk interfere, it becomes necessary to examine their extent with precision.

The following table shows the *linear dilatation of glass** and several of the metals between the freezing and the boiling-point of water.

1000000 of Glass tube . become	1000861	1000000 of Copper . become	1001712
„ Crown Glass „	1000875	„ Brass . . „	1001783
„ Platinum . „	1000856	„ Silver . . „	1001890
„ Cast iron . „	1001111	„ Tin . . . „	1001937
„ Steel . . . „	1001189	„ Lead . . „	1002867
„ Gold . . . „	1001460		

The expansion in *volume* may be obtained without sensible error by

* In reference to the irregularities in the expansion of glass of different kinds and in different forms, see REGNAULT, *Ann. Ch. et Ph.*, 3 Ser. iv. 64.

trebling the number which expresses the increase in *length*, where, as in the above cases, the fraction of its length is small.

In the range of temperature between 32° and 212°, these expansions are apparently nearly equable; but the experiments of Dulong and Petit (*Ann. Ch. et Ph.*, and *Ann. of Philos.*, xiii. 164), prove that the rate of expansion increases with the temperature, as shown in the following tables:—

I. *Increasing Dilatation of Glass by Heat.*

Temperature by Air Thermometer.	Mean absolute Dilatation of Glass for each Degree.	Temperature by a Thermometer made of Glass.
From 32° to 212°	$\frac{1}{6\ 9\ 6\ 6\ 0}$	212°·0
„ 32° to 392°	$\frac{1}{6\ 5\ 3\ 4\ 0}$	415°·8
„ 32° to 572°	$\frac{1}{5\ 9\ 2\ 2\ 0}$	667°·2

II. *Increasing Dilatation of Metals by Heat.*

Temperature by Air Thermo- meter.	Mean Dila- tation of Iron for each Degree.	Temperature by Iron-rod Thermo- meter.	Mean Dila- tation of Copper for each Degree.	Temperature by Copper Thermo- meter.	Mean Dila- tation of Platinum for each Degree.	Temperature by Platinum Thermo- meter.
212°	$\frac{1}{5\ 0\ 7\ 6\ 0}$	212°	$\frac{1}{3\ 4\ 1\ 2\ 0}$	212°	$\frac{1}{6\ 7\ 8\ 6\ 0}$	212°
572°	$\frac{1}{4\ 0\ 6\ 7\ 8}$	702°·5	$\frac{1}{3\ 1\ 8\ 6\ 0}$	623°·8	$\frac{1}{6\ 5\ 3\ 4\ 0}$	592°·9

It appears that, at temperatures beyond 212°, glass expands in a greater ratio than mercury, and as the mercurial thermometer measures the *difference* of the expansion of the glass and metal upon the supposition that they are both uniform, its degrees require a correction in the upper part of the scale, when compared with equal dilatations of air. Thus the temperature of 586° on the mercurial thermometer corresponds with 572° on the air thermometer; while, from the third column of the first table, it appears that the expansion of glass alone, supposed to be equable, would indicate 667° for the same point. The second, fourth, and sixth columns of the second table show the mean expansion for each degree, of iron, copper, and platinum when heated from 32° to 212°, compared with that from 32° to 572°; the third, fifth, and seventh columns indicate the degrees on thermometric bars of these metals, corresponding to the temperature of 572° on an air thermometer. By the aid of his pyrometer, Daniell constructed the following table, showing the progressive amount of the expansion of several metals, up to their point of fusion. (*Introd*, § 149.)

Progressive Dilatation of Solids. 1000000 parts at 62°.

	At 212°.	At 662°	At Fusing Point.
Black Lead Ware	1000244	1000703	
Wedgwood Ware	1000735	1002995	
Platinum	1000735	1002995	1009926 maximum, but not fused.
Iron (Wrought)	1000984	1004483	{ 1018378 to the fusing points of cast iron.
Iron (Cast)	1000893	1003943	1016389
Gold.....	1001025	1004238	
Copper.....	1001430	1006347	1024376
Silver	1001626	1006886	1020640
Zinc.....	1002480	1008527	1012621
Lead.....	1002323		1009072
Tin.....	1001472		1003798

According to Ure, *zinc* permanently elongates after frequent heating and cooling. "It would seem," he says, "that the plates composing this metal, in sliding over each other, by the expansive force of heat, present such an adhesive friction as to prevent their entire retraction." In regard to the unequal expansion of bodies at different temperatures, he remarks, that it is probable every species of matter follows an increasing rate in its enlargement by heat, for each portion that enters a body must weaken cohesion, and therefore render the operation of the next portion that is introduced more efficacious." The curious fact of the unequal expansion of certain crystals discovered by Mitscherlich has already been mentioned, (p. 12.)

The force exerted by the calorific expansion of solids is familiarly illustrated by the cracking of thick glass vessels, and especially flat plates of glass, when suddenly or irregularly heated, as when hot water is poured into a common tumbler, or when a thick-bottomed flask is placed upon the sandheat: the heated surface is expanded, and in consequence of the bad conducting power of the material as well as of its mechanical texture, the heat can only slowly make its way to the next layer, so that the different parts of the vessel are thrown into different states of tension, and a fracture is the consequence: these accidents may be avoided by using very thin vessels, or by the very gradual application of the heat: in selecting flasks and retorts, we should therefore obtain them as thin as is consistent with safety, and above all avoid those with blebs, or of unequal thickness. We sometimes avail ourselves of the expansive effect of heat upon glass in cutting off parts of vessels, by causing a crack to follow the direction of a red-hot wire traced upon the surface: common watch-glasses are in this way cut out of a glass globe, and various cracked glasses made useful in the laboratory. (FARADAY'S *Chem. Manip.*)

Flat plates of cast iron are especially liable to be cracked by sudden changes of temperature, or by unequal expansion; the backs of grates, and the dampers of flues are thus frequently broken: they are less liable to these accidents when slightly curved.

In consequence of the extensive use which is made of iron in the construction of bridges, and as a substitute for timber, architects have become more fully aware of the necessity of making due allowance for its expansion and contraction, and such arrangements as may admit of it without injury to the other parts of the building. The arches of the Southwark bridge rise and fall about one inch within the usual range of atmospheric temperatures. Where great lengths of iron pipe are used, as for the conveyance of gas or water, some of the junctions are so contrived as to allow of their elongation and contraction, without fracture. Where iron beams are employed, they must be so placed as to admit of some play without injury to the walls; and where such precaution has not been taken, their contraction and expansion have tended to endanger the building. Iron roofs, in consequence of their situation exposing them to the influence of a hot sun, or to the cold of winter, require peculiar care in this respect; and in other cases, apparently of trivial importance, serious consequences have resulted from the incautious application of iron bars in situations where their changes of bulk could be productive of mischief, as in clamping stones together in the construc-

tion of steeples, and in placing iron railings between columns, &c.; for these changes of bulk, small as they are in amount, take place with irresistible force. This fact was well illustrated in an application made of it by Molard for restoring the perpendicularity of the walls of the Museum of Arts and Manufactures in Paris, which, in consequence of the weight of the roof, were bulging outward; he laid iron rods across the building, the ends of which projected through the opposite walls; these rods were then heated, and when in an expanded state, a strong iron plate upon either end of each rod was firmly screwed up against the exterior of the wall: during their contraction on cooling, the rods drew the walls somewhat nearer together: the bars were then again elongated by heat, the screws being again tightened, and so by a repetition of the process the walls were gradually brought to a perpendicular position. The same process has been applied in the restoration of the cathedral at Armagh.

It appears from the preceding table (p. 27) that the expansion of glass and of platinum is nearly similar: hence wires of that metal may be welded into fused glass without inconvenience; but if we substitute a wire of another metal, its different rate of contraction will tend to break the glass as it cools. It is also seen that iron or steel is less expansible than brass; if, therefore, we form a compound bar of these or any other two differently expansible metals, by riveting or soldering them together, such a bar, by changes of temperature, will constantly warp in one direction or



other, according to the relative position of the steel and brass. Let fig. 56 represent the compound bar, the steel being uppermost; if we then put it upon a heated plate, the bar will warp, as shown in fig. 57, in consequence of the greater expansion of the brass; if,

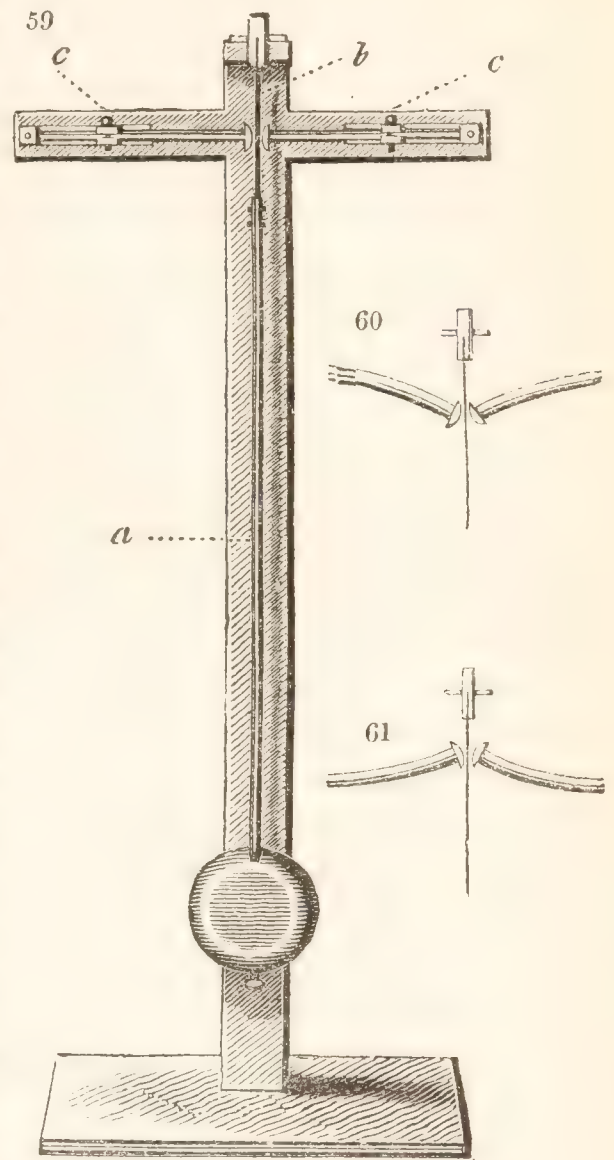
on the contrary, the compound bar be subjected to cold, it will assume the opposite curve (fig. 58), in consequence of the greater contraction of the brass. A compound plate of silver and platinum is remarkably susceptible of these contortions; and such contrivances have been applied to the construction of instruments for measuring changes of temperature, as in *Breguet's Thermometer*, which consists of a very thin and narrow strip of platinum, plated with silver and coiled into a spiral, one end of which is attached to an upright support, and the other to an index moving over a graduated circle: with changes of temperature the spiral twists and untwists, carrying with it the index: the value of the degrees on the circle is determined by comparison with a mercurial thermometer.

The expansion and contraction of metals by heat and cold is a serious inconvenience to the chronometer-maker, as necessarily interfering with the rate of going of the clock or watch. The pendulum, to vibrate seconds, must always be of a given length*, and it is obvious that if of metal it will be liable to shorten in winter and lengthen in summer: thus the clock will be fast in the former, and slow in the latter season†.

* The length of the pendulum vibrating seconds in *vacuo* in the latitude of London (51° 31' 8" North) at the level of the sea, and at the temperature of 62°, is = 39.13929 inches of Sir George Shuckburgh's standard scale. KATER, *Phil. Trans.*, 1819, p. 415.

† When the bob is let down $\frac{1}{100}$ of an inch, the clock loses ten seconds in twenty-

The contrivances which have been resorted to, to counteract this inconvenience, are numerous, and many of them extremely ingenious; but any details upon the subject would be misplaced here. The following mode of compensation is, however, particularly illustrated by the principle here explained. *a* represents the pendulum-rod of brass or steel, suspended by the thin plate *b* between the compensation-bars of brass and steel (fig. 56) *c c*, which are firmly fixed at the ends *c*, and supplied with proper adjustments. Let us now suppose the pendulum exactly vibrating seconds at the temperature of 62° , and that the temperature rises to 80° : in this case, the bar *a* would be elongated, and it would not then vibrate so many as 60 seconds in the minute; but the effect of increase of temperature in the compensation-bars, supposing the brass uppermost, would be to warp them, as in the annexed sketch, fig. 60, and, virtually, to shorten the pendulum; and in cold weather, on the contrary, the rod of the pendulum would be shortened, but the bars warping upwards (as in fig. 61,) would tend to elongate it. A similar plan of compensation may be applied to the balance-springs of watches, which are affected in the same way, and with the same effects, as the pendulum of a clock.



The dimensions of wood are much less altered by changes of temperature than those of metals; certain kinds of wood, therefore, are occasionally used for the rods of large pendulums, but wood is liable to be deranged by the varying moisture of the atmosphere. A slip of marble has also been used as a pendulum-rod.

There are some common operations, in which the expansion and contraction of metals by heat and cold are beneficially applicable: by putting the hoops upon a cask, in a heated state, they gradually contract on cooling, and firmly bind the staves together; and, with the same view, the wheelwright heats the tire of his wheel, that it may firmly press upon the circumference as it cools: so also the plates of large boilers are united by hot rivets, which during their contraction on cooling draw them firmly and securely together.

A remarkable anomaly as regards the usual laws of expansion and contraction is presented by the fusible alloy of two parts of bismuth, one of lead, and one of tin. A bar of this metal at 32° expands till it attains the temperature of 111° ; it then contracts by the continued

four hours; hence the elongation of $\frac{1}{1000}$ | to 30° of Fahrenheit will alter its length
of an inch will cause it to lose one second | about $\frac{1}{3000}$ part, and occasion an error in the
per day, and a change of temperature equal | rate of going, of eight seconds per day.

addition of heat up to 156° , when it has attained its maximum density, occupying less space than even at 32° ; it then again progressively expands, its point of fusion being 201° . (ERMANN.) These phenomena are well illustrated by filling a glass test-tube with the fused alloy, and suffering it to cool; this goes on quietly till it arrives at its minimum volume, 156° ; soon after which the tube is suddenly broken by the expansion of the metal during cooling, it attaining its maximum volume at 111° . Graham observes in regard to this alloy, that as it is a chemical compound of a kind in which a change of constitution is very likely to occur from a change of temperature, its peculiarities cannot fairly be compared with those of *water* presently to be noticed. (See BISMUTH.)

§ 3. EXPANSION OF LIQUIDS.

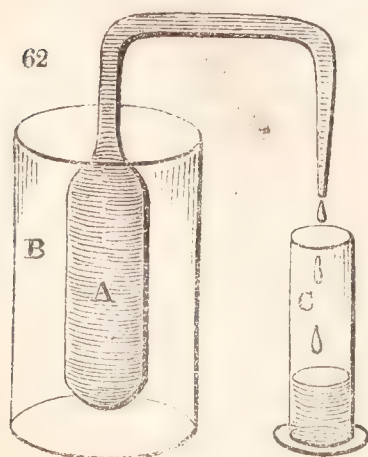
THE expansibility of different liquids, like that of solids, is liable to variation: alcohol, for instance, is more expansible than ether, and ether than water, and water than mercury. Liquids are also differently expansible at different temperatures; and, generally speaking, their rate of expansion increases with their temperature. This irregularity is chiefly observed in those liquids which readily boil; where they require a very high temperature to convert them into vapour, it is less observable. The expansion of mercury, for instance, at low and high temperatures, is only slightly dissimilar; hence one of its advantages in the construction of thermometers.

The following are the rates of expansion of several liquids on being heated from 32° to 212° .

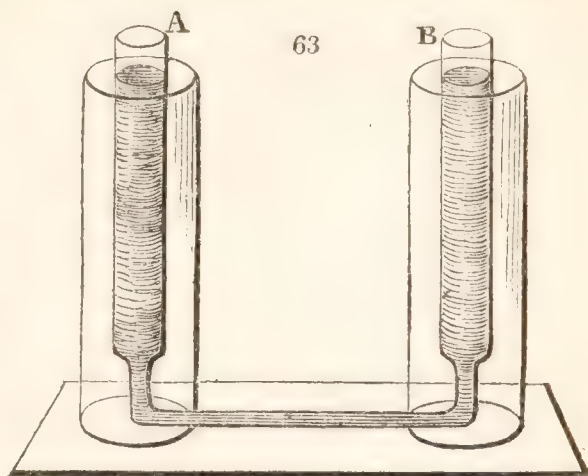
Alcohol	expands	$\frac{1}{9}$,	that is	9 measures become	10
Sulphuret of Carbon	„	$\frac{1}{9}$	„	9	10
Nitric Acid (Sp. Gr. 1.45)	„	$\frac{1}{9}$	„	9	10
Fixed Oils	„	$\frac{1}{12}$	„	12	13
Ether	„	$\frac{1}{14}$	„	14	15
Oil of Turpentine	„	$\frac{1}{14}$	„	14	15
Sulphuric Acid	„	$\frac{1}{17}$	„	17	18
Water	„	$\frac{1}{22.76}$	„	22.76	23.76
Mercury	„	$\frac{1}{55.5}$	„	55.5	56.5

Alcohol, therefore, is six times more expansive by heat than mercury: and in the height of summer spirit of wine will measure about 5 per cent. more than in the depth of winter.

The amount of the expansion of liquids may be most conveniently measured by introducing them into a small glass flask A, the neck of which is drawn out as in the annexed figure: this may be filled with the liquor at any given *low* temperature and its weight determined; it may then be immersed into the water or oil-bath B, and heated up to any given *high* temperature, by which a quantity of the liquid will be expelled into c. When cold the flask may be removed from the bath, wiped clean and dry, and again weighed, when the loss will give the proportion of expansion. But as, in consequence of the expansion sustained by the bulb or flask A, a result some-



what below the real expansion will thus be indicated, it is sometimes necessary to make a correction on that account: the actual expansion of mercury, for instance, between 32° and 212° , is about $\frac{1}{55}$ th of its volume, whereas its *apparent* expansion in the above experiment would only amount to about $\frac{1}{67}$ th. With very expansible liquids the amount of this error will of course be very trifling; but it may be avoided by the use of the apparatus of Dulong and Petit the principle of which is shown in the annexed cut (fig. 63); they heated the



liquid in one limb of a syphon, A, and observed how high it rose above the level of the same liquid in the other limb, B, the temperature of which was uniform. The amount of expansion was calculated from the difference of level in the limbs read off upon a graduated scale. (For the details of the construction and use of their apparatus see *Ann. Ch. et Ph.*, vii. 127.)

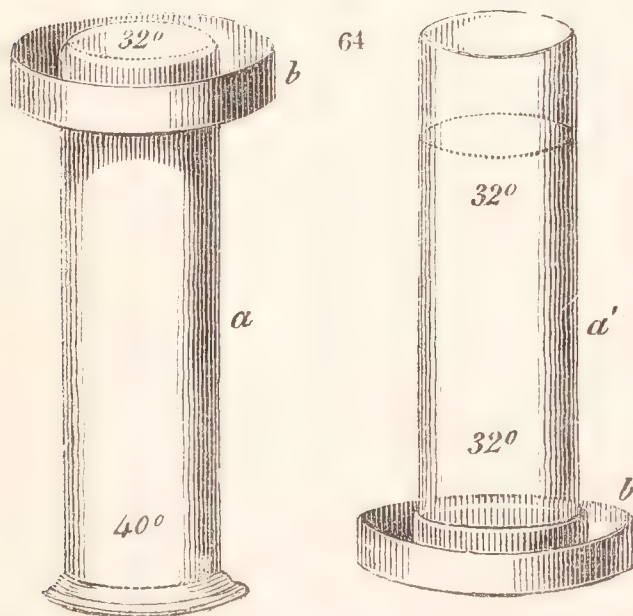
The expansibility of the liquids resulting from the compression of gases is extremely remarkable, for it appears from the experiments of Thilorier (*Ann. Ch. et Ph.*, LX. 427) that liquid carbonic acid is even more expansible by heat than air; heated from 32° to 86° , twenty volumes of this liquid increase to twenty-nine, which dilatation is about four times greater than that of air. Kemp has extended this observation to the liquids resulting from the compression of sulphurous acid and of cyanogen, which, though less dilatable than carbonic acid, are much more so than common liquids.

There is an extraordinary exception to the law of expansion and contraction by heat and cold, in the case of *water*, which, unlike other fluids, *expands when cooled below a certain point*. Other fluids diminish in bulk till they freeze; but if we fill a large thermometer-tube with water, of the temperature, for instance, of 80° , and then plunge the bulb into a freezing mixture, the water goes on shrinking till it has attained the temperature of about 40° ; and then, instead of continuing to contract till it freezes, (as is the case with other liquids,) it slowly expands and rises in the tube until it congeals. In this case the expansion below 40° and above 40° seem to be equal; so that water will be of the same bulk at 32° as at 48° , that is, at 8° degrees above or below 40° . Crichton's experiments place the maximum of density at 42° , (*Ann. of Phil.*, N.S., v., p. 491;) those of Hallström at 39.4 . (*Ann. Ch. et Ph.* xxviii., p. 90.) There is an elaborate paper in the *Ann. Ch. et Ph.* (t. LXX.) by Despretz, upon the maximum density of water and of saline solutions; he places the maximum density of water at $+4^{\circ}$ Centigrade, (about 39.5° Fahr.,) and states that below the maximum density the dilatation by cold is more considerable than the dilatation by heat above the same point, but that the difference is very minute and may probably be fallacious: that sea water and all saline solutions have a maximum of density: that the maximum of density sinks more rapidly than the point of congelation.

This anomalous expansion of water by cold is productive of important consequences in nature; for if water, like other fluids, went on diminish-

ing in bulk, and therefore increasing in density, till it froze, large bodies of water, instead of being only superficially frozen in winter, would become solid masses of ice. Let us take a fresh-water lake as an example. The earth being warmer in winter than the air, the heat is withdrawn from the *surface* of the water by the cold breezes that blow over it, and the whole body of water has its temperature lowered to 40° , *which is the point of its greatest density*, and a temperature congenial to fish and other aquatic animals. The cold now continues to operate upon the surface of the water, but instead of diminishing its bulk, and rendering it *heavier* than the warmer water beneath, it expands and renders it *lighter*; so that, under these circumstances, a stratum of ice-cold water (at 32°) will be found lying upon a mass of warmer water beneath it (at 40°). The influence of the cold continuing, the surface of the lake will soon freeze, but the water immediately below the superficial coating of ice will be found comparatively warm; and as water is almost a non-conductor of heat, it will be a long time before the ice attains any thickness; and the whole body of water, if of any depth, can never freeze throughout. Indeed, it will be obvious that in the case we have supposed, the retardation of freezing will be proportional to the depth of water which has to be cooled, and hence some very deep basins or lakes are scarcely ever covered with ice.

Perhaps the following experiment may render this property of water more intelligible. Let $a\ a'$, fig. 64, represent two cylindrical vessels, filled with water at 50° ; $b\ b'$ are iron trays surrounding and closely fitting the exteriors of the cylinders, and intended to contain a freezing mixture of snow and salt, which in a is applied to the upper *surface*, but in a' to the *bottom* of the water. When the temperature of the whole bulk of water, in both vessels, is reduced to 40° , that is, to the point of

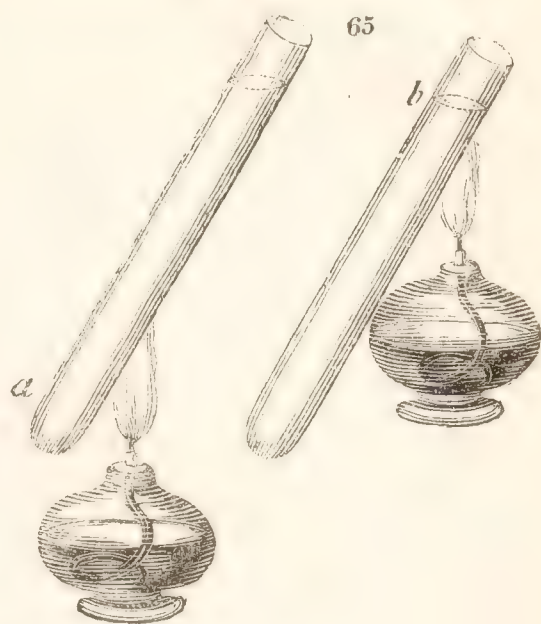


greatest density, it will be found that, in the vessel a , the cooling effect will not proceed downwards, but will be limited to the surface, where the thermometer will gradually fall to 32° , and the water probably freeze; for the ice-cold water being lighter than the water at 40° below, it will necessarily float upon the surface: a thermometer, therefore, in the upper part of the vessel will fall to 32° , but in the lower part only

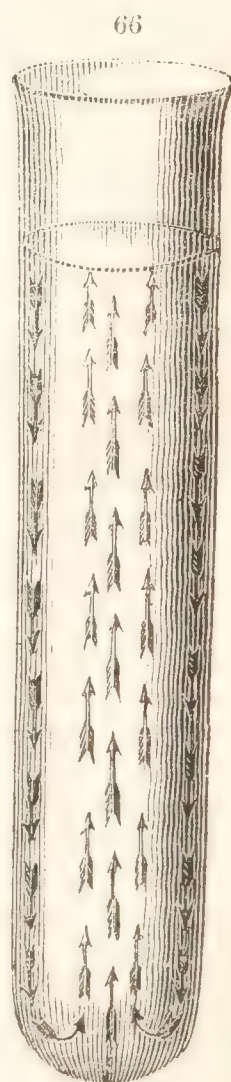
to 40° . This may be said to represent the case of the lake above described. In the second cylinder a' , the cold, instead of being applied to the surface of the water, is applied to the bottom, and the effect is very different; for now the cooled water becoming lighter, ascends, whilst the warmer water descends, and becoming cooler in its turn, the whole body of water is reduced to the freezing temperature, an effect limited to the *surface* in the other cylinder, which represents what happens in nature, where the cold is always superficial; and ice being lighter than water, it is, of course, formed and remains upon the surface.

As liquids, generally speaking, are *enlarged*, and consequently ren-

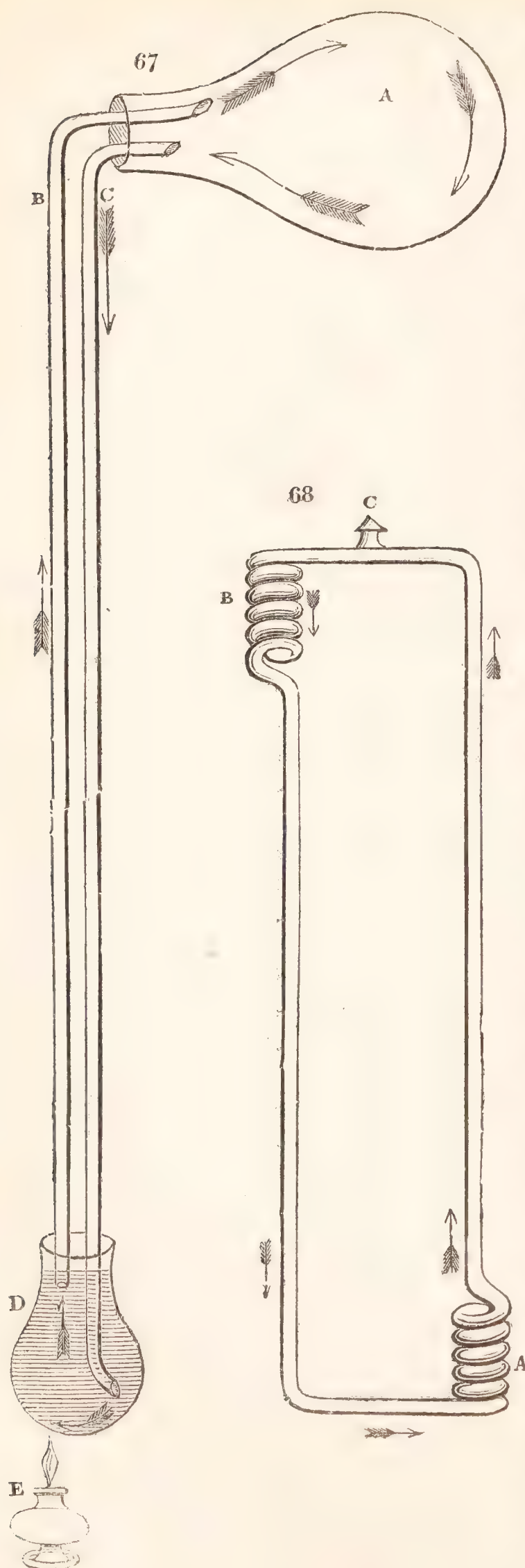
dered *specifically lighter*, by heat, it follows that, in heating a mass of liquid, very different effects will be produced by applying heat to different parts of the vessel containing it: *a* and *b*, fig. 65, represent two tubes of thin glass filled with water. If we apply the flame of the spirit-lamp to the *bottom* of the tube *a*, the water will soon be heated equally throughout, and boil; and this is the usual way of applying heat, namely, to the bottom of the boiler; but if, as in the tube *b*, we heat the *surface* of the water, it may be made to boil in the upper part, whilst at bottom it will remain cold. In this case, the water becomes *lighter* by being heated, and consequently floats upon the colder water below, to which scarcely any heat will be communicated.



The *currents* that ensue, in the ordinary way of heating water, may be rendered obvious by the following experiment:—Fill a cylindrical glass vessel, of the shape annexed, fig. 66, with water, and throw into it a few particles of bruised amber, or any other convenient substance, nearly of the same specific gravity as the water, so that, if possible, they may neither sink nor float in it; then apply a gentle heat to the centre of the *bottom* of the vessel, and it will be seen that currents immediately begin to ascend in the centre, or axis, and to descend towards the circumference of the vessel, in the direction shown by the darts, or in an inverted direction if the *sides* of the tube are most heated. These currents soon become rapid, and continue till the water boils. It is, therefore, by changes in the density of the different portions of water, that we succeed in diffusing heat (by what has been termed *convection*) throughout the mass. The heated portion becomes enlarged, and, therefore, specifically lighter than the adjacent cold portions through which it ascends; whilst they, descending, come into the contact of the heated surface, and in their turn expand and rise. This goes on till the whole of the water has acquired its boiling temperature, and the currents then cease.



Such currents may be established, in properly-constructed vessels, to any extent, and heat thus communicated to water at a considerable distance from the boiler; a system advantageously adopted in heating houses, conservatories, manufactories, and baths. The contrivances for these purposes are very various; but all, of course, imply the necessity of an *ascending* and *descending* current. The annexed (fig. 67) is a form of apparatus for the illustration of the direction and extent of these currents, and their application to the conveyance of heat from one place to another. *A* is a large glass flask filled with water, into which the tubes *B C* are tightly



fitted by a perforated cork and cement ; these tubes are also filled with water, and dip into the flask D, which is filled with water deeply tinged blue with indigo ; the tube B dipping only about half an inch below the surface, whilst C descends nearly to the bottom of the blue liquor, and should be very slightly curved upwards at its extremity. On applying the flame of a spirit lamp, as at E, the blue liquid ascends by the tube B, and circulates through A, the water from which descends through C into D, and thus a circulation of the fluid is kept up, and the heat conveyed from one flask to the other.

In Perkins's apparatus for conveying heat through buildings by the circulation of water, an endless tube is employed, the surface of which is occasionally increased by spiral or other turnings where the heat is to be given off or acquired : the annexed figure (68) may serve to illustrate this principle ; it represents a strong wrought iron tube of about one inch diameter completely filled with water ; the spiral A passes through a furnace where it is highly heated, and the water is consequently put into motion in the direction of the arrows ; the boiling of the water or formation of steam is prevented by the pressure, whence the necessity of the extreme perfection and strength of the tube. B represents a second coil which is supposed to be in an apartment where the heat is to be given out. C is

a screw stopper by which the water may be occasionally replenished. By this form of apparatus the water may be heated to 300° or 400° , or

even higher, so as occasionally to singe paper. A larger tube and lower temperature are, however, generally preferable*.

§ 4. EXPANSION OF AËRIFORM BODIES AND VAPORS.

THESE undergo much greater relative changes of bulk than the other forms of matter, but they also present an important peculiarity. In other substances, each individual has its own degree of expansion and contraction, whereas *all pure aëriform bodies expand and contract alike*: so that, if we accurately determine the expansion and contraction of any one of them, in a given range of temperature, that knowledge applies to all the rest. It has been ascertained by Dalton and Gay Lussac that 1000 measures of dry air, when heated from the freezing to the boiling-point of water, suffer an increase in bulk about equal to 375 parts; so that 1000 cubic feet of air, at 32° , become dilated to 1375 cubic feet at 212° †. Air, therefore, at the freezing-point, expands $\frac{1}{480}$ th part of its bulk for every added degree of heat on Fahrenheit's scale: that is,

480	cubic inches,	at 32° ,	become
481	—	at 33° ,	
482	—	at 34° , &c.	

increasing one cubic inch for every degree. A contraction of one cubic inch occurs for every degree below 32° : thus

480	cubic inches,	at 32° ,	become
479	—	at 31° ,	
478	—	at 30° , &c.	(GRAHAM.)

The volume of air, therefore, at 32° would be doubled at 480° , and tripled at 960° : the latter temperature being about that of a dull red heat. Steam, and all other vapors, when heated out of contact of their respective fluids, are subject to laws of expansion similar to those of air.

It may be remarked in regard to the expansion sustained by aëriform bodies by increase of temperature, that, although great in amount, the actual force which is thus exerted, is small (as compared with that of solids and liquids under the same circumstances), in consequence of their extreme elasticity: thus, although the volume of air (or of vapor) is about tripled by a red heat, vessels are easily found which sustain

* A question has been raised concerning the safety of Perkins's apparatus, not merely as relates to the danger of explosion, but also respecting that of high temperature; and it has been asserted that the water may be so highly heated in the tubes as to endanger the charring and even inflammation of paper, wood, and other substances in their contact or vicinity: such no doubt might be the case in an apparatus expressly intended for such purposes, but in the apparatus as constructed by Perkins, with adequate dampers and safety valves, and used with common care, no such result can ensue. Paper bound round an iron tube is not affected till the temperature exceeds 400° ; from 420° to 444° it becomes brown or slightly singed; sulphur does not inflame below 540° .

† Rudberg (POGGEND. *Ann.*, xlii.) places this increase at between 364 and 365 parts; and Regnault, in an elaborate memoir on the dilatation of gases published in the *Ann. Ch. et Ph.*, 3me Serie, t. iv., p. 5, arrives at the conclusion that 1000 parts of air at 0° Centigrade (32° Fahr.) become 1366 at 100° (212° Fahr.) He also finds the coefficients of dilatation of nitrogen, hydrogen, and oxygen, to agree exactly with that of air: but carbonic acid, protoxide of nitrogen, and cyanogen, present under the same circumstances a higher number, that of carbonic acid being 0.3685. (See also papers on this subject by Magnus, *Ann. Ch. et Ph.*, 3 S., vi. 330 and 353, and remarks on them by Regnault, *ibid.*, 370.) According to James Crichton, 1000 volumes of air at 32° become 1374.8 at 212° .

the pressure of the included elastic fluid, and it is only where atmosphere is successively added to atmosphere (as where a portion of liquid is simultaneously present) that the pressure mounts up to a dangerous extent.

Thomson has given the following tabular view of the bulk of 100,000 parts of air at all temperatures between 32° and 212°

Temp.	Bulk.	Temp.	Bulk.	Temp.	Bulk.	Temp.	Bulk.	Temp.	Bulk.
32°	100000	49°	103536	65°	106864	81°	110192	97°	113520
33	100208	50	103749	66	107072	82	110400	98	113728
34	100416	51	103952	67	107280	83	110608	99	113936
35	100624	52	104166	68	107488	84	110816	100	114144
36	100833	53	104368	69	107696	85	111024	110	116224
37	101040	54	104576	70	107904	86	111232	120	118304
38	101248	55	104791	71	108112	87	111440	130	120384
39	101459	56	104992	72	108320	88	111648	140	122464
40	101666	57	105200	73	108528	89	111856	150	124544
41	101872	58	105408	74	108736	90	112064	160	126624
42	102080	59	105616	75	108944	91	112272	170	128704
43	102290	60	105824	76	109152	92	112480	180	130784
44	102496	61	106032	77	109360	93	112688	190	132864
45	102703	62	106240	78	109568	94	112899	200	134944
46	102916	63	106448	79	109776	95	113104	210	137024
47	103124	64	106656	80	109984	96	113312	212	137440
48	103333								

The rate of expansion of atmospheric air at temperatures *above* 212° has been investigated by Dulong and Petit (*Ann. Ch. et Ph.*, vii. 120). The following table exhibits the results of their observations.

Temperature by the Mercurial Thermometer.		Corresponding Volumes of a given Volume of Air.
Fahr.	Centig.	
— 33	— 36	0·8650
32	0	1·0000
212	100	1·3750
302	150	1·5576
392	200	1·7389
482	250	1·9189
572	300	2·0976
680	360	2·3125

The dilatation suffered by air, when heated, being very considerable, is, of course, attended by a proportionate diminution in the specific gravity or relative weight of the heated portion, which ascends through the colder mass, and excites currents and agitations in the general bulk of air. These currents often escape observation, in consequence of the invisibility of air; but they may easily be rendered evident; and often excite attention by their violence, as when powerful draughts and wind are produced. The smoke-jack is put into motion by the force of the current of air which passes up the chimney.

In consequence of this relative *lightness* of heated air, it always rises to the upper parts of rooms and buildings, when it either escapes, or, becoming cooled and relatively *heavier*, again descends. If, in cold weather, we sit under a skylight in a warm room, a current of cold air is felt descending upon the head, whilst warmer currents, rising from our bodies, and coming into contact with the cold glass, impart to it their excess of heat. Being thus contracted in bulk, and rendered specifically heavier, they, in their turn, descend, and thus a perpetual motion is kept up in the mass of air, an effect attended with much inconvenience to those who inhabit the room, and in great measure prevented by the use of double windows.

We generally observe, when the door of a room is opened, that there are two distinct currents in the aperture, which may be rendered evident by holding in it the flame of a candle. At the upper part it is blown outwards, but inwards at the lower part; in the middle, scarcely any draught of air, one way or other, is perceptible.

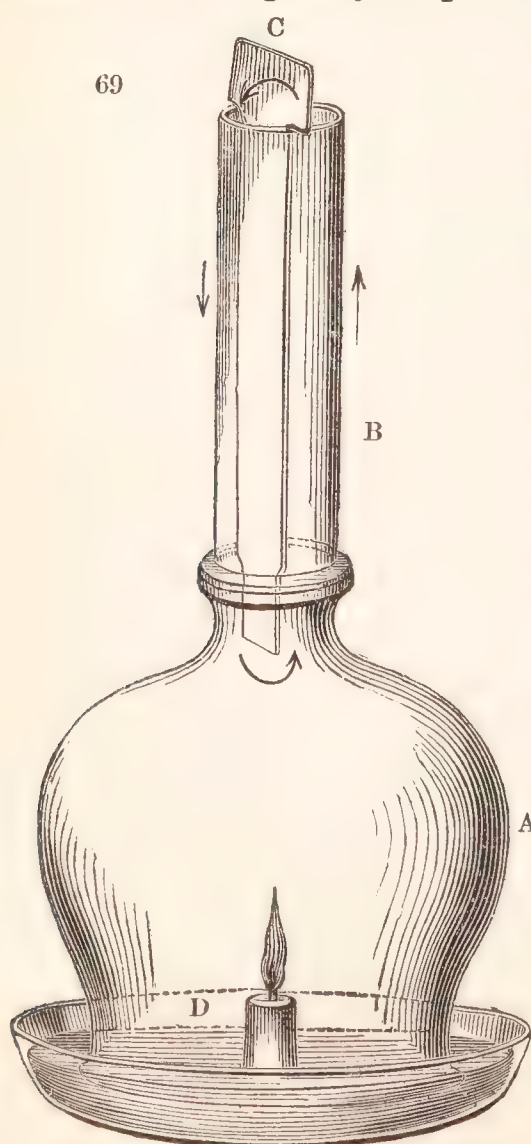
The art of ventilating rooms and buildings is, in a great measure, dependent upon the currents which we are enabled to produce in air by changes of temperature, and is a subject of considerable importance. As the heated air and effluvia of crowded rooms pass upwards, it is common to leave apertures in or near the ceiling for their escape. Were it not, indeed, for such contrivances, the upper parts of theatres and of some other buildings would scarcely be endurable; but a mere aperture, though it allows the foul air to escape, in consequence of its specific lightness, is also apt to admit a counter-current of denser and cold air, which pours down into the room; and this almost always happens where there is no free ingress of air into the lower part of the apartment, so that in some cases heated air will ascend by one half of the aperture, and cold air descend by the other. Such an effect may be prevented by heating, in any convenient way, the tube or flue through which the foul air escapes. A constantly ascending current is then established; and whenever cold air attempts to descend, the heat of the flue rarefies and drives it upwards. Thus the different ventilators may terminate in tubes connected with a chimney; or they may unite into a common trunk, which may pass over a furnace purposely for heating it; or heated air may be sent, by a flue from below, into the space between the roof and ceiling of the room to be ventilated, and it may have free escape by proper apertures.

In some of our theatres, the gas-chandelier is made a very effectual ventilator. It is suspended under a large funnel, which terminates in a cowl outside the roof; the gas-burners heat the air considerably, and cause its rapid and constant ascent through the funnel, connected with which there may be other apertures in the ceiling of the building. But in these and similar cases, we often observe that the vents are not sufficiently capacious; and the foul air from the house, and from the gas-burners themselves, not being able readily to escape, diffuses itself over the upper part of the building, and renders the galleries hot and suffocating, all which is easily prevented by the judicious adjustment of the size of the ventilating channels to the quantity of air which it is requisite should freely pass through them. The small ventilators, consisting of a rotating wheel, which we sometimes see in window-panes, are perfectly useless, though it is often imagined, in consequence of their apparent activity, that they must be very effectual; but the fact is, that a trifling current of air suffices to put them in motion, and the apertures for its escape are so small as to produce no effectual change in the air of the apartment: they are also as often in motion by the ingress as by the egress of air.

From what has been said, it will be obvious that our common fires and chimneys are powerful ventilators, though their good services in this respect are often overlooked. As soon as the fire is lighted, an ascending current of air is established in the chimney, and consequently there must be a constant ingress of fresh air to supply this demand, which generally enters the room through the crevices of the doors, windows, and floor.

When these are too tight, the chimney smokes; and in such cases it is sometimes necessary to make an aperture in some convenient part of the room for the requisite admission of air, or to submit to sitting with a window or door partly open. Any imperfect action of the chimney, or descending current, is announced by the escape of smoke into the room, and is frequently caused by the flue being too large, or not sufficiently perpendicular and regular in its construction. When there is no fire, the chimneys also generally act as ventilators; and in summer there is often a powerful current up them, in consequence of the roof and chimney-pots being heated by the sun, and thus accelerating the ascent of the air.

In a well-constructed house, there should be sufficient apertures for the admission of the requisite quantity of air into the respective rooms, without having occasion to trust to its accidental ingress through every crack and crevice that will allow it to pass. These openings may either be concealed, or made ornamental, and, by proper management, may be subservient to the admission of warm air in winter. A few spare flues should also be provided, independent of the chimneys, which may be used either for the egress or ingress of air, as occasion may require. Where there is no other provision for access of air, it often happens that a current descends by one chimney to ascend by another, as is commonly observed where two rooms communicate, and where a fire in one of them is supplied by the sooty air which descends the chimney of the other. These cases of double currents may be strikingly illustrated as follows:—A is a glass jar open at bottom and top, and standing in a dish or



plate, which, if necessary, may contain a little water, so as to seal the lower aperture: a glass cylinder B, is placed upon the upper aperture so as to form a kind of chimney in which a vertical diaphragm of glass or card C, is so placed as to divide it into two channels. When matters are thus arranged, a lighted candle placed at D, will continue to burn, the foul air passing upwards, and fresh air downwards, as shown by the darts on either side of the diaphragm. But if the diaphragm be removed, the candle will presently burn dimly or be extinguished, inasmuch as the distinct ascending and descending currents will then be prevented; and in order to support combustion, it will be necessary to admit air from below, under the edge of the bell glass. The direction of the currents may be shown by holding a piece of smoking paper, or the glowing wick of a green wax taper over the respective sides of the chimney.

The manner in which heat is distributed through our apartments by the fires in common use, will be noticed afterwards; but large rooms are not uncommonly warmed by heated air, admitted usually through apertures in

the floor. This system is convenient, effective, and agreeable, when properly managed, but this is seldom the case. The rooms are close and oppressive, because due *ventilation* is not associated with the admission of the hot air; the apertures by which the air is admitted are generally too small, and the air itself overheated: the openings should be, according to circumstances, either large, or very numerous, and the *quantity* of air thrown in should be *considerable*, but its *temperature moderate*. In this way the bad smell produced by burnt particles of dust is avoided, and an agreeable freshness, as well as temperature, kept up in the air.

§ 5. OF THE DETERMINATION OF SPECIFIC GRAVITIES.

FROM the changes of bulk which bodies sustain when they change their temperature, it is obvious that their relative *densities or specific gravities* will be liable to proportionate changes; hence chemists are in the habit of referring these to the mean temperature of 55° or 60° , and as the bulk of aëriiform bodies is also subject to change by increased or diminished pressure, their densities are compared not only at mean *temperature*, but also at mean *barometrical pressure*.

By the term *specific gravity*, we mean the ratio of *weight* to *bulk*; the object, therefore, of the processes for ascertaining it, is either to determine the *weight of a known bulk*, or the *bulk of a known weight*; for whether the substances be reduced to the same weight, and then measured, or to the same bulk, and then weighed, the ratio of their weights to their bulks will be discovered. If reduced to the same bulk, and weighed, their specific gravities will be *directly* as the weights; if reduced to the same weight and measured, their specific gravities will be *inversely* as their bulks. Suppose a like bulk of each kind of matter in nature to be weighed, the results, numerically stated, would represent their specific gravities. But as this would be inconvenient, and often impossible, another method of reducing their bulks to a common measure is resorted to; and, in the case of solids and liquids, pure water is assumed as the unit to which their specific gravities are compared. On dividing the weight, for instance, of any bulk of the metal *zinc* by the weight of a like bulk of water, the quotient is 7; this, therefore, is said to be the specific gravity of zinc. Proceeding in the same way with *silver*, the quotient is 10.47; with *gold*, 19.3; with *potassium*, 0.86; with *sulphuric acid*, 1.84; with *alcohol*, 0.80: hence these numbers are considered as representing the specific gravities of those bodies; that is, they are their relative weights to water, all being of the same temperature. To obtain the specific gravity, therefore, of a body, we divide its weight by the weight of a quantity of pure water equal to it in bulk, and this we determine as follows:—

We use a delicate balance*, so contrived as to admit of substances

* Balances fitted up for the purpose of ascertaining specific gravities are sold by the philosophical instrument makers: in regard to their use, and the precautions requisite in the various steps of the process, see FARADAY'S *Manipulation*, § II.

“Equality in the length of the arms of the lever is, of course, the most important consideration in the construction of the

balance; but when there may be any reason to doubt this essential point, it is well to know that any error may be avoided by the method of *double weighing*. This consists in placing the object whose weight is to be ascertained in one scale-pan and exactly counterbalancing it in the other, not with the weights, but with sand or shot, or any other indifferent substance. The substance

being attached to one of the scales by means of a horse-hair or a fine thread of silk. The absolute weight of the body thus suspended is then carefully ascertained: it is next immersed in distilled water, of the temperature of 60° ; and the beam being again brought to an equilibrium, we learn the weight lost by its immersion; or, in other words, we ascertain the weight of its bulk of pure water. We now divide the sum of its absolute weight by that of the weight which it lost in water, and the quotient is its *specific weight*, or gravity, compared with water of the temperature of 60° .

Suppose a substance weighing 360 grains, to lose 60 by immersion in water, the specific gravity of that substance will be $= 6$; for $360 \div 60 = 6$.

When the substance, whose specific gravity is to be ascertained, is *lighter* than water, it may be suspended with some heavier body, and, having determined the weight of the former in air, and of the latter in water, we fasten them together by means of a fine thread (not so closely as to exclude water from their contiguous surfaces, or to include air-bubbles), and weigh them in water, when it will be found that their aggregate weight will fall short of that of the heavier body. If we now subtract the weight of the lighter body from that of the heavier body, and add the remainder to the weight of the former in air, we obtain the weight of a quantity of water equal in bulk to the lighter body; we then divide the weight of the lighter body in air by this last-mentioned sum, and the quotient is its specific gravity.

"A piece of elm wood, having been varnished over to prevent its absorbing water, was found to weigh 920 grains in *air*; a piece of lead, chosen as the ballast, was ascertained to weigh 911.7 grains in *water*; the elm and lead were then tied together, and were found to weigh, in *water*, only 331.7 grains, being 580 grains less than the weight of the lead alone; therefore 580 were added to 920, that is, to the weight of the elm in air, which made up the sum of 1500: lastly, 920 were divided decimally by 1500, and the quotient .6133, gave the specific gravity required."—(PARIS, *Med. Chem.* 9.)

When the substance, whose specific gravity is required, is *soluble* in water, some other fluid, of known specific gravity, must be used, which does not act upon it; alcohol, oil of turpentine, or olive oil, may, in most instances, be used, or in some cases the substance may be coated with varnish. The following is an illustration of this mode of weighing. Supposing the density of crystallized sugar to be required, and the fluid selected to be oil of turpentine of the specific gravity of 0.87, the sugar is first weighed in air, and then in the oil; the difference gives the weight of an equal bulk of the oil; then, if the weight of the sugar in air be 400 grains, and its weight in oil of turpentine 182.5, the weight of an equal bulk of the oil will be $400 - 182.5 = 217.5$. Then $0.87 : 100 :: 217.5 : 250$, and $400 \div 250 = 1.6$, which is the specific gravity of

is then removed, and the weights applied in the same pan till the counterpoise is balanced. By this contrivance the unknown quantity of matter is compared with the known, under exactly equal circumstances, and the result is independent of almost every source of error which can

affect the comparison. An object may also be correctly weighed in an incorrect balance, by changing the object and the weights from one pan to the other; the mean of the two weighings may be mathematically proved to be correct."—DANIELL, § 32.

the sugar. When the substance is in small pieces or *powder*, it may generally be weighed in the specific-gravity bottle used for liquids.

For ascertaining the specific gravity of liquids, we may employ a thin phial, holding 1000 grains of distilled water, at the temperature of 60° . If filled with any other liquid, and weighed, we learn its specific gravity; thus we should find that it would contain 13·500 grains of mercury; 1845 grains of sulphuric acid; 1420 grains of nitric acid, &c., which numbers of course represent the specific gravities of those liquids.

A bottle, however, holding 1000 grains, is often inconveniently large, and a small and thin globular phial, with a piece of thermometer-tube ground into it by way of stopper, will be found more useful: such a phial should not weigh more than from 50 to 60 grains, and may contain between 400 and 500 grains of water. To use it, it should be accurately counterbalanced in a delicate pair of scales, and then filled with distilled water, and the stopper thrust in, the capillary opening in which allows a little to ooze out, and prevents the likelihood of bursting the phial; it is then to be wiped clean and dry, and again carefully weighed, by which the quantity of water it contains is ascertained; the water being poured out, it is next filled with the liquid whose specific gravity is required, taking care that it is of the same temperature as the water; we then weigh as before, and divide the weight of the liquid by the former weight of water; the product gives the specific gravity required. Thus, suppose the phial to contain 425 grains of water at the temperature of 60° , it will be found to hold 5737·5 grains of pure mercury of the same temperature; and $5737\cdot5 \div 425 = 13\cdot5$, the specific gravity of mercury. Or, supposing the liquid lighter than water, such as spirit of wine, of which we may assume the phial to contain 350·5; then $350\cdot5 \div 425 = 0\cdot824$, the specific gravity of the spirit under trial.

Another mode of determining the density of a fluid is founded on the above stated fact of a solid displacing its own bulk of liquid: take a glass bulb the loss of weight of which when immersed in water is known, and, weighing it in any other fluid, again ascertain its loss: this latter divided by its loss in water will be the required specific gravity. Supposing, for instance, that the bulb lost 30 grains in water and 24 grains when weighed in alcohol, then $24 \div 30 = 0\cdot800$, the specific gravity of the alcohol, for $30 : 1000 :: 24 : 800$.

We also, in determining the specific gravity of fluids, frequently employ the *hydrometer*, an instrument constructed upon the principle that solids of a given weight sink deeper in light than in heavy fluids; it cannot, however, be resorted to where great accuracy is required, but where a number of specific gravities are to be quickly determined, as in respect to spirituous liquors for the purpose of levying duties, or in certain processes of the arts, these instruments, from the facility of their application, become indispensable. (See ALCOHOL.)

The determination of the specific gravity of air, and of different gases and vapors, will be described under the article *Atmospheric Air*, as it involves several circumstances not yet adverted to.

§ 6. THERMOMETERS AND PYROMETERS.

HAVING stated some of the general effects of contraction and expansion, we may now proceed to the examination of the *thermometer*—an

instrument of considerable importance in researches connected with the subject of heat. As ordinarily constructed, it is in fact a very delicate fluid measure, capable of indicating with great accuracy the *bulk* of the included liquid.

70



The first instrument to which the term *thermometer* (from *θερμος*, *heat*, and *μητρον*, *a measure*) can properly be applied, was apparently invented by the Florentine Academicians, about the middle of the seventeenth century. It consisted of a glass tube, with a bulb or ball blown at one extremity (fig. 70), and filled up to a certain mark, with spirit of wine; the *expansion* of which, or its rise *above* the mark, indicated *heat*, and its *contraction*, or fall *below* the mark, *cold*. They afterwards placed a number of equidistant studs of white enamel on the tube, rendering the expansions and contractions of the confined liquid more evident; and by these they sometimes divided it into a hundred parts or degrees. Such instruments were first introduced into England by Boyle. For a long time, no one would believe that a liquid could contract and expand in a tube closed at both ends; but Boyle soon satisfied himself of the fact by experiment, and by the inspection of the *Florentine glasses*, for so these instruments were then called.

About the beginning of the eighteenth century a considerable improvement was made in this original thermometer, by Fahrenheit, of Amsterdam, who, by the use of mercury instead of alcohol, was enabled greatly to diminish the size of the tube and bulb, and to measure comparatively high degrees of temperature.

But these instruments laboured under the serious defect of entire want of agreement with each other: the division of the tube was founded on no fixed principle, but was arbitrary, and differently constructed and applied in every thermometer. It required no common ingenuity to overcome this difficulty, and to construct instruments which should agree with each other when exposed to the same temperature. This, however, was at length effected by a suggestion of Newton, founded upon a discovery of Hooke, who observed, that when a thermometer-tube, properly filled with mercury, was plunged into melting ice or snow, the liquid metal always contracted, or fell to a certain point, at which it remained perfectly stationary till all the ice was melted. If we now mark this point upon the tube, it will be found that, whenever it is subjected to the same experiment, the quicksilver falls exactly to the same level or point, and hence this point may be called the *melting-point of ice*; and it has since been ascertained that this is also precisely the point at which water, under ordinary circumstances, freezes, so that it is also called the *freezing-point of water*. Here, then, a part at least of the difficulty above adverted to is removed, and *one* fixed point for thermometric graduation ascertained.

Dr. Hooke afterwards made a similar discovery in regard to boiling water, which, under ordinary circumstances, he found always exhibited one and the same degree of heat. If, therefore, we now plunge the thermometer, upon which the freezing-point of water has already been marked, into an open vessel of water placed upon the fire or over a lamp, we shall observe the mercury continue to rise in the tube until the water boils,

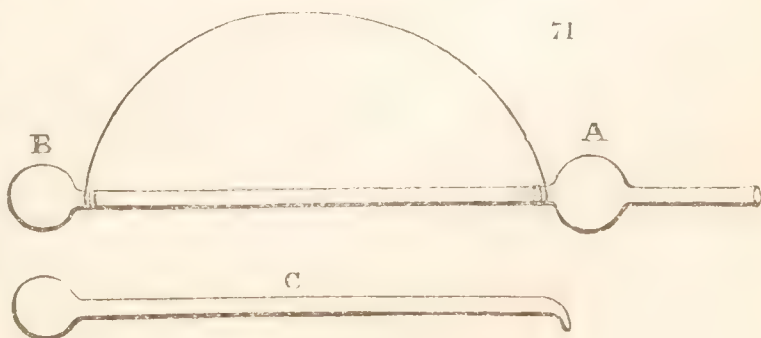
when it becomes quite stationary, and the point may be marked as before. Now it will be found, that whenever this thermometer is put into boiling water, the mercury will rise to the same height*. Here, then, we have a *second* determinate point, namely, *the boiling-point of water*; and it is now obvious, that if we divide the space of the tube between these two fixed points into any given number of degrees, the mercury will indicate the same degree in all bodies of one and the same temperature; and that any number of thermometers, carefully constructed upon this principle, will agree with each other in their indications of temperature.

The space between the boiling and freezing of water has often been divided into *one hundred* equal parts—the freezing-point being marked 0° , and the boiling-point 100° . This is commonly called the *centigrade scale*; it originated with Celsius in Sweden, and is used in France and many other parts of Europe. *Reaumur's scale* calls the freezing-point 0° , and the boiling-point 80° , and is employed in most parts of Germany and Italy. In this country we generally use *Fahrenheit's scale*, which sets out at the temperature produced by mixing snow with salt, which is 32° below the freezing of water; and the space between that and the boiling-point being divided into 180° , the latter is called 212° . In all these scales, the graduation is continued below 0° in the same way as above it. These are called *degrees below 0°* , and are generally distinguished by prefixing the mark (–) *minus* before them: thus -10° means ten degrees below 0° ; sometimes the mark (+) *plus* is prefixed to the degrees above zero, as $+10^{\circ}$, or ten degrees above 0° †.

* Some circumstances, afterwards to be noticed, affect the boiling-point, such as the state of the barometer or of the pressure of the atmosphere, and the nature of the vessel in which the experiment is made. We presume above that the barometer stands at thirty inches, and that the vessel is of thin and clean metal.

† The following is an abridged account of the mode of constructing a thermometer, as described by Graham (*Elements of Chem.*, p. 13):—A tube is selected, the bore of which may be of any convenient size, but must be *uniform*; this is ascertained by drawing up a little mercury into it, and progressively propelling it along the tube, measuring it as it proceeds, so as to determine that it occupies the same length throughout: one extremity of the tube is then blown into a bulb, not by the mouth, but by air propelled from a caoutchouc bag, so as to avoid the introduction of moisture: the intended length of the thermometer is then marked off, and above that point a second bulb is blown, as represented in the figure. The open end of the tube is then plunged into pure and well boiled mercury, and one of the bulbs heated so as to expel the air; as it cools the mercury rises into the ball A, and by turning the instrument and heating the bulb B the mercury passes into

that bulb as it cools: when this is full, and a portion left in A, the tube is suspended by a wire over a charcoal fire, so as to boil the mercury, by the vapour of which all moisture and air are expelled: the open end of the tube, which must not be too hot, is then touched with sealing-wax so as to close it, and the thermometer removed from the fire and held with the sealed end upward, so that during cooling the bulb B, and a portion of the tube, may be filled with mercury. After cooling the instrument is inclined a little, and, by warming the lower ball, a portion of mercury is expelled from it, so that it may stand at a proper height when the instrument is cold. The tube is then carefully melted in the blow-pipe flame below the ball A, so as to seal it as in c. (For some details upon the subject of graduation, when extreme accuracy is required, see *Ann. Ch. et Ph.*, v. 428, 3rd Ser., note.)



Fahrenheit.	Centigrade.	Reaumur.	De Lisle.
210	100	80	0
200			10
190	90		
		70	20
180			
	80		30
170		60	
			40
160	70		
			50
150		50	
	60		60
140			
			70
130	50	40	
			80
120			
	40		90
110		30	
			100
100	30		
			110
90		20	
			120
80	20		
		10	130
70			
	10		140
60			
	0	0	150
50			
			160
40	10		
		10	170
30			
20			
10			
0			

Each degree of Fahrenheit's scale is equal to four-ninths of a degree on Reaumur's: if, therefore, the number of degrees of Fahrenheit's scale, above or below the freezing of water, be multiplied by 4, and divided by 9, the quotient will be the corresponding degree of Reaumur.

Fahrenheit.

Reaumur.

$$68^{\circ} - 32^{\circ} = 36 \times 4 = 144 \div 9 = 16^{\circ}$$

$$212^{\circ} - 32^{\circ} = 180 \times 4 = 720 \div 9 = 80^{\circ}$$

To reduce the degrees of Reaumur to those of Fahrenheit, they are to be multiplied by 9, and divided by 4.

Reaumur.

Fahrenheit.

$$16^{\circ} \times 9 = 144 \div 4 = 36^{\circ} + 32^{\circ} = 68^{\circ}$$

$$80^{\circ} \times 9 = 720 \div 4 = 180^{\circ} + 32^{\circ} = 212^{\circ}$$

Every degree of Fahrenheit is equal to five-ninths of a degree on the Centigrade scale; the reduction, therefore, is as follows*:

Fahrenheit.

Centigrade.

$$212^{\circ} - 32 = 180 \times 5 = 900 \div 9 = 100^{\circ}$$

Centigrade.

Fahrenheit.

$$100 \times 9 = 900 \div 5 = 180 + 32 = 212^{\circ}$$

The annexed scale, (including De Lisle's thermometer, which is sometimes used in Russia, and in which the boiling-point is marked 0° , and the freezing 150°) shews the relation which the degrees bear to each other, and the table on the opposite page, of Fahrenheit's degrees compared with those of the Centigrade and Reaumur's scale, will save the trouble of calculation.

It is to be regretted that these discrepant thermometric scales are retained; the Centigrade or Celsius' scale is perhaps that which it would be most convenient generally to adopt. To avoid the inconvenience of the magnitude of its degrees, and the consequent necessity of frequent reference to their fractional parts, a scale has been proposed, the extremes of which are the freezing and boiling-points of mercury, the former to be 0° , the latter 1000° . The entire novelty of such a scale is its principal objection.

For all common purposes ordinary thermometers are sufficiently accurate; but the experimental laboratory should be furnished with a *standard thermometer*, very carefully constructed, and with a scale exhibiting the divisions of Reaumur, Fahrenheit,

and Celsius. Such an instrument of reference is useful to determine the quality of *common* thermometers, no two of which will be found precisely to agree at the different points of the scale.

It sometimes happens that a thermometer originally correct will after a time be found to err slightly in excess in its indications of temperature, an effect probably arising from the continued pressure of the atmosphere upon the bulb, by which its bulk is permanently diminished: this may,

* $100^{\circ} \text{ C.} = 180^{\circ} \text{ F.}; 10^{\circ} = 18^{\circ}; 5^{\circ} = 9^{\circ}.$

Fah.	Reaum.	Cent.	Fah.	Reaum.	Cent.	Fah.	Reaum.	Cent.	Fah.	Reaum.	Cent.
212	80	100	148	51.5	64.4	84	23.1	28.8	20	-5.3	-6.6
211	79.5	99.4	147	51.1	63.8	83	22.6	28.3	19	-5.7	-7.2
210	79.1	98.8	146	50.6	63.3	82	22.2	27.7	18	-6.2	-7.7
209	78.6	98.3	145	50.2	62.7	81	21.7	27.2	17	-6.6	-8.3
208	78.2	97.7	144	49.7	62.2	80	21.3	26.6	16	-7.1	-8.8
207	77.7	97.2	143	49.3	61.6	79	20.8	26.1	15	-7.5	-9.5
206	77.3	96.6	142	48.8	61.1	78	20.4	25.5	14	-8	-10
205	76.8	96.1	141	48.4	60.5	77	20	25	13	-8.4	-10.5
204	76.4	95.5	140	48	60	76	19.5	24.4	12	-8.8	-11.6
203	76	95	139	47.5	59.4	75	19.1	23.8	11	-9.3	-11.1
202	75.5	94.4	138	47.1	58.8	74	18.6	23.3	10	-9.7	-12.2
201	75.1	93.8	137	46.6	58.3	73	18.2	22.7	9	-10.2	-12.7
200	74.6	93.3	136	46.2	57.7	72	17.7	22.2	8	-10.6	-13.3
199	74.2	92.7	135	45.7	57.2	71	17.3	21.6	7	-11.1	-13.8
198	73.7	92.2	134	45.3	56.6	70	16.8	21.1	6	-11.5	-14.4
197	73.3	91.6	133	44.8	56.1	69	16.4	20.5	5	-12	-15
196	72.8	91.1	132	44.4	55.5	68	16	20	4	-12.4	-15.5
195	72.4	90.5	131	44	55	67	15.5	19.4	3	-12.8	-16.1
194	72	90	130	43.5	54.4	66	15.1	18.8	2	-13.3	-16.6
193	71.5	89.4	129	43.1	53.8	65	14.6	18.3	1	-13.7	-17.2
192	71.1	88.8	128	42.6	53.3	64	14.2	17.7	0	-14.2	-17.7
191	70.6	88.3	127	42.2	52.7	63	13.7	17.2	-1	-14.6	-18.3
190	70.2	87.7	126	41.7	52.2	62	13.3	16.6	-2	-15.1	-18.8
189	69.7	87.2	125	41.3	51.6	61	12.8	16.1	-3	-15.5	-19.4
188	69.3	86.6	124	40.8	51.1	60	12.4	15.5	-4	-16	-20
187	68.8	86.1	123	40.4	50.5	59	12	15	-5	-16.4	-20.5
186	68.4	85.5	122	40	50	58	11.5	14.4	-6	-16.8	-21.1
185	68	85	121	39.5	49.4	57	11.1	13.8	-7	-17.3	-21.6
184	67.5	84.4	120	39.1	48.8	56	10.6	13.3	-8	-17.7	-22.2
183	67.1	83.8	119	38.6	48.3	55	10.2	12.7	-9	-18.2	-22.7
182	66.6	83.3	118	38.2	47.7	54	9.7	12.2	-10	-18.6	-23.3
181	66.2	82.7	117	37.7	47.2	53	9.3	11.6	-11	-19.1	-23.8
180	65.7	82.2	116	37.3	46.6	52	8.8	11.1	-12	-19.5	-24.4
179	65.3	81.6	115	36.8	46.1	51	8.4	10.5	-13	-20	-25
178	64.8	81.1	114	36.4	45.5	50	8	10	-14	-20.4	-25.5
177	64.4	80.5	113	36	45	49	7.5	9.4	-15	-20.8	-26.1
176	64	80	112	35.5	44.4	48	7.1	8.8	-16	-21.3	-26.6
175	63.5	79.4	111	35.1	43.8	47	6.6	8.3	-17	-21.7	-27.2
174	63.1	78.8	110	34.6	43.3	46	6.2	7.7	-18	-22.2	-27.7
173	62.6	78.3	109	34.2	42.7	45	5.7	7.2	-19	-22.6	-28.3
172	62.2	77.7	108	33.7	42.2	44	5.3	6.6	-20	-23.1	-28.8
171	61.7	77.2	107	33.3	41.6	43	4.8	6.1	-21	-23.5	-29.4
170	61.3	76.6	106	32.8	41.1	42	4.4	5.5	-22	-24	-30
169	60.8	76.1	105	32.4	40.5	41	4	5	-23	-24.4	-30.5
168	60.4	75.5	104	32	40	40	3.5	4.4	-24	-24.8	-31.1
167	60	75	103	31.5	39.4	39	3.1	3.8	-25	-25.3	-31.6
166	59.5	74.4	102	31.1	38.8	38	2.6	3.3	-26	-25.7	-32.2
165	59.1	73.8	101	30.6	38.3	37	2.2	2.7	-27	-26.2	-32.7
164	58.6	73.3	100	30.2	37.7	36	1.7	2.2	-28	-26.6	-33.3
163	58.2	72.7	99	29.7	37.2	35	1.3	1.6	-29	-27.1	-33.8
162	57.7	72.2	98	29.3	36.6	34	0.8	1.1	-30	-27.5	-34.4
161	57.3	71.6	97	28.8	36.1	33	0.4	1.5	-31	-28	-35
160	56.8	71.1	96	28.4	35.5	32	0	1	-32	-28.4	-35.5
159	56.4	70.5	95	28	35	31	-0.4	-1.1	-33	-28.8	-36.1
158	56	70	94	27.5	34.4	30	-0.8	-1.5	-34	-29.3	-36.6
157	55.5	69.4	93	27.1	33.8	29	-0.3	-1.6	-35	-29.7	-37.2
156	55.1	68.8	92	26.6	33.3	28	-1.7	-2.2	-36	-30.2	-37.7
155	54.6	68.3	91	26.2	32.7	27	-2.2	-2.7	-37	-30.6	-38.3
154	54.2	67.7	90	25.7	32.2	26	-2.6	-3.3	-38	-31.1	-38.8
153	53.7	67.2	89	25.3	31.6	25	-3.1	-3.8	-39	-31.5	-39.4
152	53.3	66.6	88	24.8	31.1	24	-3.5	-4.4	-40	-32	-40
151	52.8	66.1	87	24.4	30.5	23	-4	-5			
150	52.4	65.5	86	24	30	22	-4.4	-5.5			
149	52	65	85	23.5	29.4	21	-4.8	-6.1			

however, be prevented by giving the bulb a certain degree of thickness, although the sensibility of the instrument to sudden changes of temperature is by this somewhat impaired.

It has been shown by Regnault that two thermometers which correspond at 32° , and even at 212° , do not correspond at much higher temperatures, unless made of the same kind of glass (*Ann. Ch. et Ph.*, 3^{me} Serie, iv.); and the same cause slightly affects the correspondence of the dissimilar thermometers at lower temperatures. (PIERRE, *Ann. Ch. et Ph.* 3^{me} Ser. v. 427.)

The advantages of mercury as a thermometric fluid have already been adverted to; its rate of expansion at different temperatures being more nearly equable than that of other liquids: thus Dulong and Petit found that from 1° to 100° Centigrade (32° to 212° Fahr.) it expanded 1 measure on 55.5; from 100° to 200° (212° to 392° Fahr.), 1 measure on 54.25; and from 200° to 300° (392° to 572°), 1 measure on 53. But as glass expands in a more rapidly increasing ratio than mercury, its greater expansion at the high points of the scale is corrected by the increasing capacity of the glass bulb.

There are numerous and useful varieties in the *forms* of thermometers, which need not be here enumerated in detail. Among them the *self-registering* thermometers are valuable, as showing the maximum and minimum of temperature during the absence of the observer. Many of these instruments which have been suggested, are too complicated or too expensive to be generally useful; but there are two of them which are sufficiently simple, and in common use, namely, Six's thermometer (*Phil. Trans.*, vol. LXXii.); and that contrived by Dr. Rutherford (*Edinb. Phil. Trans.*, vol. iii.)

That the degrees of the thermometer actually represent equal degrees or increments of heat, is shown by a simple experiment originally suggested by Dr. Brook Taylor. It consisted in mixing together, with due precaution, equal parts of hot and cold water; and it was found that the thermometer, applied to such a mixture, indicated the arithmetical mean between the extremes. Thus, if we mix a pound of water at the temperature of 200° with a pound at the temperature of 100° , an accurate thermometer will show in the mixture the *mean* temperature of 150° .

PYROMETERS. The indications of the mercurial thermometer are obviously limited within the freezing and boiling-points of mercury. It congeals at -39° , and boils at $+662^{\circ}$; and on the moment of its congelation it shrinks so remarkably, as to have led early experimentalists into considerable errors as to the actual cold required for the purpose. When it boils, its vapour, of course, bursts the tube. Although, therefore, the range of temperature which may be accurately measured by the expansion and contraction of mercury is very extensive, it is often requisite to measure degrees of cold below its freezing-point, and of heat above its boiling-point. Pure spirit of wine, or *alcohol*, has never been frozen, and it is consequently used in those thermometers which are intended to indicate excessive degrees of cold; but no fluid has yet been found applicable to the construction of a thermometer capable of indicating higher temperatures than the boiling-point of mercury. When, therefore, a degree of heat approaching to, or exceeding dull redness, is to be measured, other methods and substances must be resorted to: instruments constructed

for this purpose are called *pyrometers*, from *πυρ*, *fire*, and *μετρον*, *a measure*.

Of these instruments, that of Daniell is the least exceptionable, and is not liable to those sources of fallacy which render the results obtained by *Wedgwood's clay pyrometer* so uncertain and equivocal*. The following is Mr. Daniell's description of his *Register pyrometer*. (*Introd. to Chem. Phil.*, § 146.)

"It consists of two parts, which may be distinguished as the register and the scale. The *register* is a solid bar of black-lead earthenware, highly baked. In this a hole is drilled, into which a bar of any metal, six inches long, may be dropped, and which will then rest upon its solid end. A cylindrical piece of porcelain, called the index, is then placed upon the top of the bar, and confined in its place by a ring or strap of platinum passing round the top of the register, which is partly cut away at the top, and tightened by a wedge of porcelain. When such an arrangement is exposed to a high temperature, it is obvious that the expansion of the metallic bar will force the index forward to the amount of the excess of its expansion over that of the black-lead, and that, when again cooled, it will be left at the point of greatest elongation. What is now required, is the measurement of the distance which the index has been thrust forward from its first position; and this, though in any case but small, may be effected with great precision by means of the *scale*.

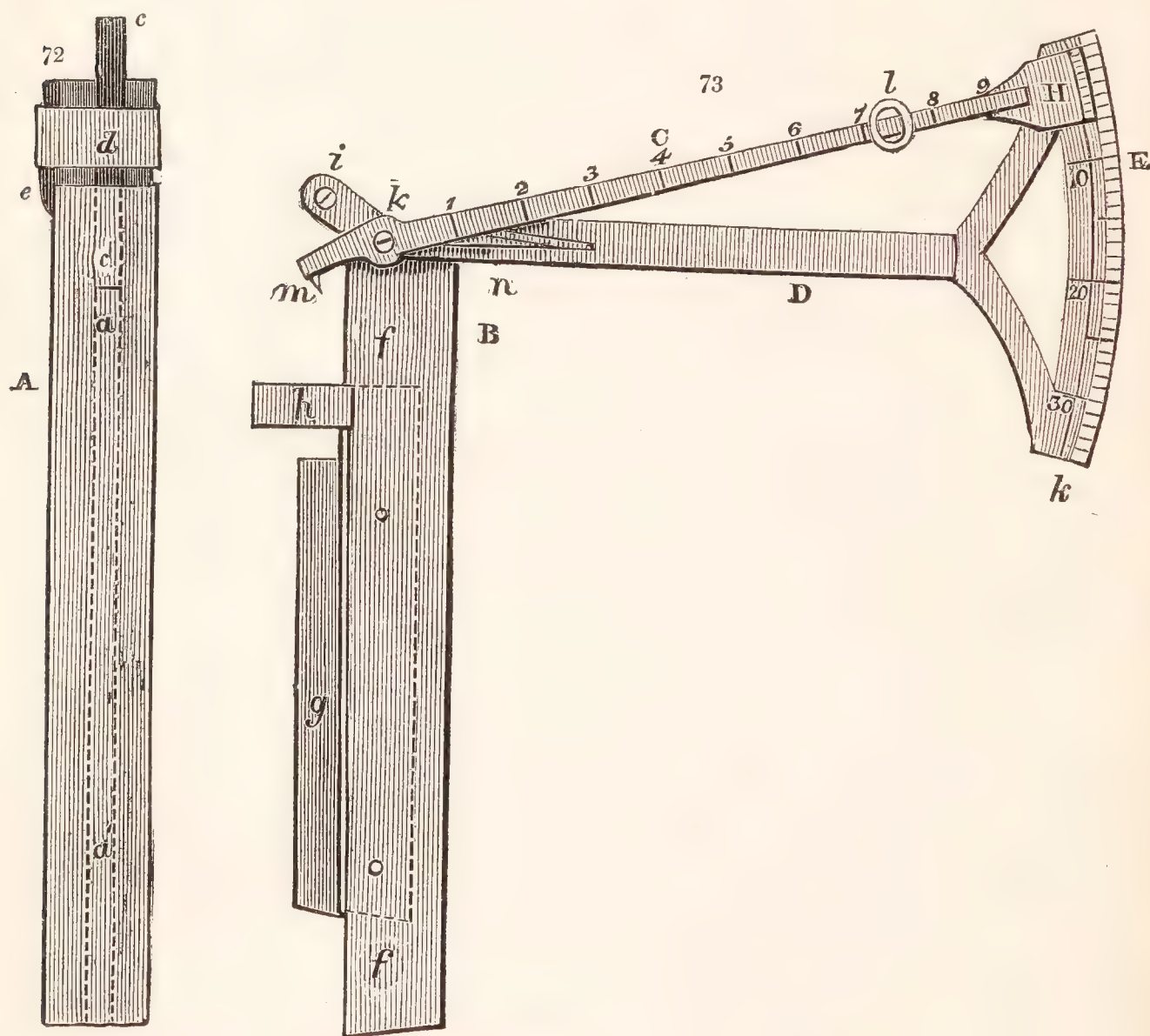
"This is independent of the register, and consists of two rules of brass, accurately joined together at a right angle by their edges, and fitting square upon two sides of the black-lead bar. At one end of this double rule a small plate of brass projects at a right angle, which may be brought down upon the shoulder of the register, formed by the notch cut away for the reception of the index. A moveable arm is attached upon this frame, turning at its fixed extremity upon a centre, and at its other, carrying an arc of a circle, whose radius is exactly five inches, accurately divided into degrees and thirds of a degree. Upon this arm, at the centre of the circle, another lighter arm is made to turn, one end of which carries a nonius with it, which moves upon the face of the arc, and subdivides the former graduation into minutes of a degree; the other end crosses the centre, and terminates in an obtuse steel point, turned inwards at a right angle.

"When an observation is to be made, a bar of platinum, or malleable iron, is placed in the cavity of the register, the index is to be pressed down upon it, and firmly fixed in its place by the platinum strap and porcelain wedge. The scale is then to be applied by carefully adjusting the brass rule to the sides of the register, and fixing it by pressing the cross piece upon the shoulder, and placing the moveable arm, so that the steel point of the radius may drop into a small cavity made for its reception, and coinciding with the axis of the metallic bar. The minute of the degree must then be noted, which the nonius indicates upon the arc. A similar observation must be made after the register has been exposed to the increased temperature which it is designed to measure,

* This pyrometer may now be considered as obsolete. It is described in the *Philosophical Transactions*, vols. Lxxii. Lxxiv. Lxxvi.

and again cooled, and it will be found that the nonius has been moved forward a certain number of degrees or minutes. The scale of the pyrometer is readily connected with that of the thermometer by immersing the register in boiling mercury, whose temperature is as constant as that of boiling water, and has been accurately determined by the thermometer. The amount of expansion for a known number of degrees is thus determined, and the value of all other expansions may be considered as proportional.

"The melting-point of cast iron has been thus ascertained to be 2786° , and the highest temperature of a good wind furnace about 3300° ; points which were estimated by Mr. Wedgwood at 20577° and 32277° respectively.



"Fig. 72 represents the register; A is the bar of black-lead; $a a'$ the cavity for the reception of the metal bar; $c c'$ is the index, or cylindrical piece of porcelain; d the platinum band, with its wedge, e .

"Fig. 73 is the scale by which the expansion is measured; $f f'$ is the greater rule upon which the smaller, g , is fixed square. The projecting arm h , is also fitted square to the ledge, under the platinum band, d . D is the arm which carries the graduated arc of the circle fixed to the rule $f f'$, and moveable upon the centre, i . c is the lighter bar, fixed to the first, and moving upon the centre, k . l is a small lens, folded back upon the arm, by which, when erected, the divisions may be accurately read off. H is the nonius at one of its extremities, and m the steel point at the other."

AIR-THERMOMETERS. Sometimes the expansions and contractions of air, which are relatively great for small changes of temperature, are resorted to in experiments in which slight variations of heat require to be indicated. The simplest form of the *air-thermometer* consists of a tube with a thin bulb at its upper end, and dipping at the lower and open extremity into a little colored fluid (fig. 74); some of the air is then expelled by the heat of the hand, so that, as the bulb cools, the liquid may rise to about half way up the tube. This instrument is very sensible to slight changes of temperature: heat expands the air in the bulb, and drives the fluid downwards; and cold, by contracting the air, causes the fluid to rise. This was one of the first forms of the thermometer that was invented, and is only inconvenient from its extreme delicacy, and the great length of tube required to measure any considerable range of heat and cold.

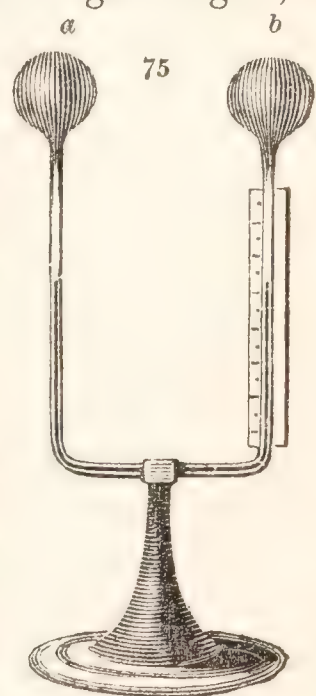
Another and more useful form of air-thermometer is represented in fig. 75: it has sometimes been called the *differential thermometer*. It consists of two bulbs, *a* and *b*, containing air, united by a tube twice bent at right angles, in which there is a little colored sulphuric acid: the tube is supported upon a wooden stand. When a hot body is brought near one of the bulbs, it expands the air within it, and drives the fluid towards the other; from *b*, for instance, to *a*. One of the chief advantages of this air-thermometer is, that it is not affected by general changes in the temperature of the surrounding air, because they act equally on both bulbs, and occasion no motion of the included column of liquid; but when one of the bulbs is exposed to any source of heat which does not affect the other, the *difference* of temperature between the two is immediately and sensibly indicated by the recession of the fluid from the heated towards the cold bulb. The advantages of this instrument will be more evident when some of its practical applications are afterwards pointed out*.

The following table will give an idea of the range of temperature within which certain points have been accurately determined: the degrees are those of Fahrenheit's scale.

Greatest artificial cold produced by Faraday	- 166°	Greatest natural cold observed by Ross	- 60°
Greatest artificial cold produced by Thilorier	- 135	Greatest natural cold observed by Parry	- 55
Solid compound of alcohol and carbonic acid fuses	- 131	Mercury freezes	- 39
Greatest artificial cold produced by Walker	- 91	Proof spirit freezes	- 7
Temperature of planetary space (Fourier)	- 58	Mixture of 1 part of alcohol and 3 of water freezes	+ 7
		Strong wine freezes	+ 20
		Ice melts	+ 32

* There is a useful treatise on the various constructions of thermometers and py-

rometers in the Library of Useful Knowledge. *Natural Philos.*, vol. ii.



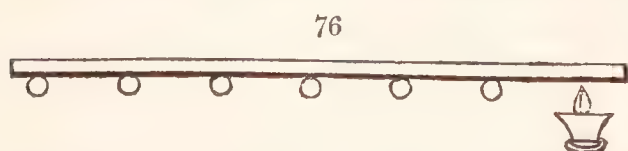
Medium temperature of the surface of the globe	+	50°	Tin melts	+	442°
Medium temperature of England	+	52	Lead melts	+	594
Heat of human blood	+	98	Mercury boils	+	662
Pyroligneous spirit boils	+	150	Red heat	(Daniell) ..	+ 980
Alcohol boils	+	174	Heat of common fire (do.) ..	+	1140
Water boils	+	212	Brass melts	(do.) ..	+ 1869
			Silver melts	(do.) ..	+ 2233
			Cast iron melts	(do.) ..	+ 3479

§ 6. CONDUCTION OF HEAT.

WE have already seen how readily heat is diffused through liquids by convection, or change of density, and that its propagation through aëriiform bodies is often dependent upon a similar mode of transfer. When heat traverses *solid* bodies its passage is altogether of a different character; it suffers great retardation, and is said to be *conducted*.

It has been observed by Herschel (*Discourse on the Study of Natural Philosophy*), that as the particles of the most solid bodies are not absolutely in contact, conduction, when properly considered, is merely a case of radiation, and “that if we would rightly understand what is the process of nature in this slow communication of heat through the substance of a solid, we must ground our inquiries upon what takes place at a distance, and then urge the laws to which we have arrived up to their extreme case.” This mutual dependence of the laws of conduction and radiation will be again adverted to when considering the latter mode of the propagation of heat; but we are too little acquainted with the minute corpuscular structure of bodies, to know what goes on between particle and particle, in apparent contact; and the bad radiating, yet good conducting power of the metals, apparently shows that these are distinct modes of the propagation of heat.

CONDUCTION BY SOLIDS. A rod or bar of metal is well calculated to illustrate this conduction of heat: if one end of it be held in the candle, and the other in the hand, the heat gradually and progressively makes its way from one end to the other; if the hand be near the source of heat, or the bar short, it soon becomes too hot to hold. This gradual progress of heat along the bar is well shown by attaching several wooden balls to the side of a square bar of metal 18 or 20 inches long, at intervals of about two inches apart, by a little wax, and then heating one end of the bar over a lamp (fig. 76); the balls successively drop off as the



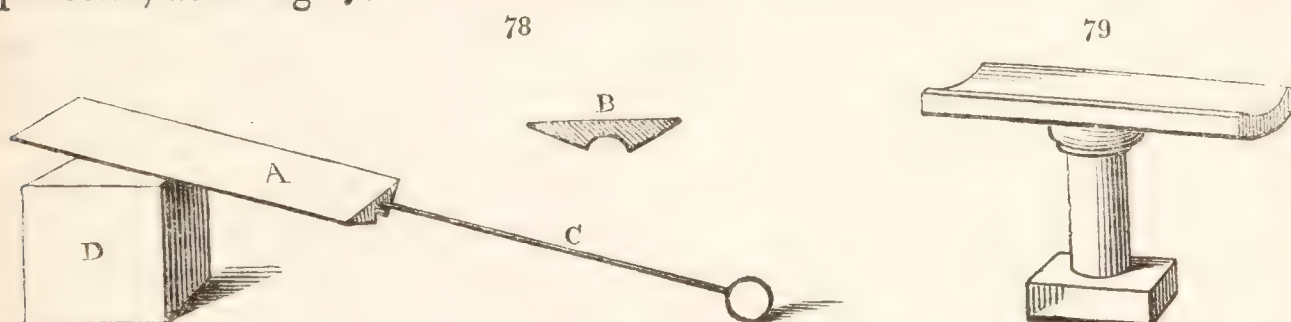
heat finds its way along the bar. If we employ bars of *different* metals, it will be found that some conduct heat better than others: thus, if two similar bars or wires, one of platinum and one of silver, be heated at one end, the heat will pervade the silver much more rapidly than the platinum; or if cones of several metals, like that represented in fig. 77, be respectively tipped with a small piece of wax, and placed upon a heated plate of metal, the wax will melt at different periods upon the different cones, thus showing their different conducting powers.



Gold, silver, and copper are the best conductors; next to these platinum, iron, zinc, and tin: lead is the worst conductor among the metals. (INGENHOUSZ, *Jour. de Phys.*, 1789, p. 68; DESPRETZ, *Ann. Ch. et Ph.*,

xix. 97.) It does not appear, therefore, that the conducting power corresponds either with the density, the tenacity, or the fusibility of the metals. In these cases of conduction the following law is observed: if the extremity of a metallic bar be placed in communication with a constant source of heat, and we wait till it has taken up a permanent state of temperature, we shall find that for distances from the source, taken in arithmetical progression, the excess of temperature above the surrounding medium will form a geometrical progression.

Trevelyan observed that when masses of metal of different temperatures and conducting powers were properly placed in contact, they produced vibratory or rapid rocking motions attended by musical sounds. (*Phil. Mag.*, N.S., iii. 321.) These vibrations are most intense when the heated metal is the best conductor, and the cold the worst: they are well observed when a heated bar of copper is placed upon a block of lead, and continue till the temperatures are equalized, (FORBES, *Phil. Trans.*, *Edinb.*, xii.,) the tones often rising and falling like those of an Æolian harp. A (fig. 78) represents a grooved bar of brass or copper about five inches long and half an inch in diameter, of which a section is shewn at B. C is a thick iron wire, with a brass knob screwed on to its end, which serves as a handle, and D the block of lead upon which the highly heated bar is placed; sometimes a curved bar is used, resting upon a leaden pedestal, as in fig. 79.



Next to metals, the diamond, the topaz, and some earthy compounds, appear to have the greatest conducting power: then stony bodies, porcelain and glass, and porous earthy compounds, such as earthenware and bricks. Wood is a very bad conductor of heat; so is charcoal; and these may be held, without burning the fingers, very near the red-hot part.

The following table, from the experiments of Despretz, (*Ann. Ch. et Ph.*, xxxvi. 422,) represents the conducting powers of several metals and other substances compared with gold.

Gold	1000	Copper	898	Tin	304	Porcelain	12
Platinum	981	Iron	374	Lead.....	180	Brick	11
Silver	973	Zinc.....	363	Marble.....	24		

But in this table, the conducting power of *platinum* is greatly over-estimated, and it will afterwards appear that it should stand much below silver and copper, and but little above iron and zinc, so that the number 381, rather than 981, would more correctly represent its conducting power in reference to gold as = 1000.

From the experiments of Mayer, of Erlangen, (*Ann. de Chim.*, xxx.,) it would appear that the conducting powers of different woods are in some measure inversely as their specific gravities, but these experiments require repetition, and certainly in many instances the least dense woods are, as might be expected, the worst conductors. (DELAIVE and DECANDOLLE, *Ann. Ch. et Ph.*, XL. 91.)

Porous substances used in clothing, and the natural coverings of most animals, are also bad conductors of heat ; but in these and similar cases interstitial air cannot be excluded, and consequently their true conducting power is not accurately determinable*. Count Rumford found that when a heated thermometer, surrounded by about an inch in thickness of confined *air*, took 576 seconds to cool 135° , it took 1032 seconds to cool to the same point when 16 grains of *lint* were diffused through the confined air, and 1305 seconds when the same weight of *eiderdown* was used ; so that if it be assumed that the conducting power is inversely as the times, if the power of air be $= 1000$, that of the lint will be $= 558$, and of the eiderdown $= 441$; there can, however, be no doubt that in these experiments the *conducting* power of the confined air is not correctly represented ; that it is greatly inferior to the solid fibres of the porous bodies experimented upon, and that in proportion as these prevent its ready change of place, they oppose the transmission of heat ; we accordingly find that the conducting power of these substances is further diminished by the closeness with which their particles are compressed, provided, that is, their texture is not too closely compacted : thus, when the same space, which in the above experiment was occupied by 16 grains of eiderdown, was filled first with 32 grains, and then with 64, the times employed in the escape of the heat from the enveloped thermometer were successively increased from 1305 seconds to 1472 and 1615 seconds. To show the influence of mere *texture* upon conducting power, similar trials were made with raw silk, ravelings of white taffeta, and of common sewing silk ; of which the first has the finest fibre, the second less fine, and the third, from being twisted and harder, is much coarser. The difference between these three modifications of the same substance was very striking ; the raw silk detaining the heat for 1284 seconds, the taffeta ravelings 1169 seconds, and the silk thread only 917 seconds. (*Phil. Trans.*, 1792.)

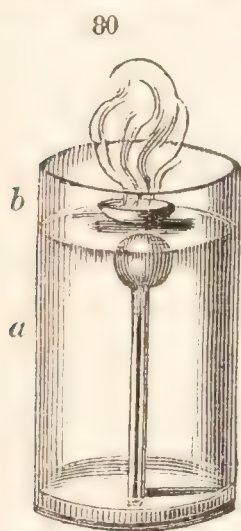
The application of these facts to the retention of the natural heat of the body by different kinds of clothing, is sufficiently obvious ; and it is evident that, as far as mere conducting power of animal and vegetable substances is concerned, the worst conductors are those in which the fibres are finest and least condensed. There are, however, other circumstances which interfere in these applications, and which will be more intelligible when the subject of *radiation of heat* is under consideration.

CONDUCTION BY LIQUIDS. Liquids are very imperfect conductors of heat, and have sometimes been regarded as non-conductors. It has already been shown, that in the usual mode of heating liquids, the heat is applied to the *bottom* of the vessel containing them, and is diffused or conveyed through the mass in consequence of successive *changes of density* in the heated portions ; the warm currents which are thus established ascend, and the cold ones descend, and this motion is kept up till the water boils. If, however, we apply heat to the *surface*

* The quantity of air included in a heap of cotton wool, for instance, and the small bulk of *substance* in it, is amusingly shown by very nearly filling a cylindrical glass vessel with alcohol (which perfectly wets the fibre and prevents the adhesion of the

air which ensues when it is put into water), and then gradually thrusting into it a large heap of the wool, of which an enormous bulk is required before the alcohol runs over the edge of the vessel.

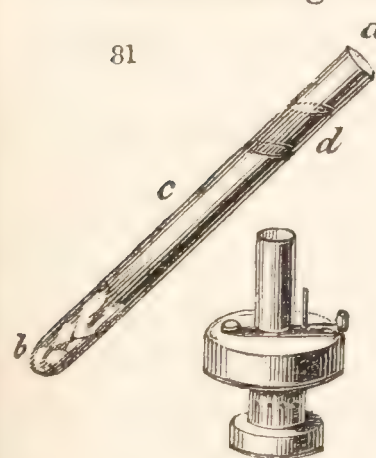
of the water, the heat can only be propagated downwards by its *conducting power*; for the heated portion, being lighter than the cold water beneath, floats upon its surface, and no interchange of strata, analogous to that previously described, can ensue. It may thus be shown that it is extremely difficult to transmit heat through water or other nonmetallic fluid by its mere conducting power. The following, among other experiments, may be selected in illustration:—Let *a*, fig. 80, represent a cylindrical vessel of water with an included air-thermometer, the bulb of which



very nearly reaches the surface: *b* is a thin copper basin floating upon the surface, the bottom of which is only separated from the bulb of the air-thermometer by a very thin stratum of water: if some inflamed ether or alcohol, or a little glowing charcoal, be now put into the basin, a film of water upon the surface may be heated to its boiling-point, and yet scarcely any elevation of temperature will be indicated by the neighbouring thermometer; and it will be impossible

to transmit the heat from the surface downwards. In this way of making the experiment, it is obvious that some heat may be conveyed by the sides of the vessel; but as glass is a bad conductor, this source of error is comparatively small, though it produces an effect when the heat on the surface is long continued.

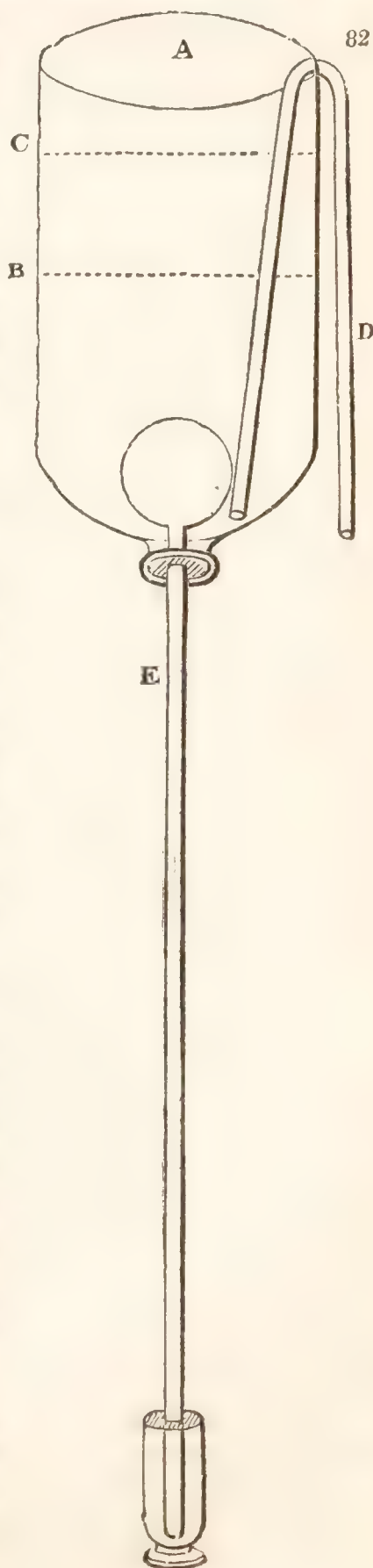
The following is a mode of illustrating the



bad conducting power of another liquid—namely *oil*. *a*, fig. 81, represents a thin glass tube about two feet in length, closed at one end, and open at the other: pour into it a couple of inches of water, and freeze it by immer-

sion in a mixture of salt and ice; then upon the lump of ice at the bottom, *b*, pour eight or ten inches of oil, *c*, and upon the oil, two or three inches of spirit of wine, *d*. If the portion of the tube containing the spirit be now carefully held over the chimney of a lamp, the spirit may be boiled, and even entirely evaporated, whilst the oil will be little heated, and the ice not thawed.

A good class-experiment upon this subject, where it is necessary that effects should be seen at a distance, may be arranged as follows:—Let *A* (fig. 82) represent a glass jar (which may be supported upon a ring-stand,)



filled up to the line B with cold water. E is a long-tubed air thermometer, fitted water-tight into the neck of the jar, the colored liquid in which stands at about the level E, the bulb being surrounded by the cold water. A thin disc of cork nearly fitting A is then floated upon the water, and some hot water tinged blue or red is carefully poured up to the level, c, when the cork disc (preventing its mixture with the cold water beneath) may be removed, and the hot colored water remains floating upon the cold colorless water, and no effect is produced upon the thermometer. The syphon, D, is now carefully introduced, and the cold water gradually drawn off, so as to allow the hot colored stratum to descend within a line of the bulb, but it still produces no effect till the hot water touches, and afterwards surrounds, the air-thermometer, when the liquid in its tube immediately descends from E into the cup.

These, and similar facts and experiments, show that *water, and most other liquids, are very imperfect conductors of heat*; and that they acquire and lose heat principally by the currents which have been above described, and which take place in them when partially heated or cooled; the warmer parts ascending, and the colder descending. Whatever impedes these motions will proportionately interfere with the heating and cooling of the fluid. Hence viscid liquids, or those containing substances that mechanically thicken them, are more tardy in their reception and emission of heat than pure water: of this, pasty fluids and thick soups afford a familiar example; they are heated with difficulty, and are a long time cooling.

The inference which has sometimes been drawn, that the state of liquidity prevents conduction, or the transfer of heat from particle to particle, is negatived, in regard to mercury at least, by substituting that metal for the cold water, in the apparatus, fig. 82; on pouring hot water upon its surface the thermometer is presently affected, even through a considerable stratum of the fluid metal.

CONDUCTION BY GASES. The experiments which have been made to determine the *conducting powers of gaseous bodies* are not very satisfactory in their results: and it has as yet scarcely been ascertained whether *aëriform bodies* are or are not *conductors* of heat. A striking illustration of the non-conducting power of *steam* is afforded by carefully dropping a little water into a silver spoon or platinum crucible, heated nearly to redness; the water lies upon the metal so long as it is prevented coming into perfect contact with it by the interposed layer of steam; but as soon as the crucible cools down, so as to admit the water to touch it, it instantly boils off. This explanation is however disallowed by M. Laurent. (*Ann. Ch. et Ph.*, lxii. 327.) See also a paper "on the Phenomena of Bodies projected upon Hot Surfaces," by M. Boutigny. (*Ann. Ch. et Ph.*, N.S., ix. 350 and xi. 16.) The mobility of a piece of solid carbonic acid upon surfaces at common temperatures, is referable to the same cause; and the difficulty of converting it into gas, even when the surface is heated, well illustrates the non-conducting power of the gas and of the solid acid.

The bad conducting power of pure flame, such as that of alcohol, is illustrated in the comparative difficulty with which it communicates heat to a bar of metal, and the finger may even be passed through it without burning. Large and clean grains of gunpowder are bad conductors, and

therefore when cautiously dropped into the flame of a spirit lamp will often not take fire; whereas fine iron-filings, being good conductors, burn in the same flame, and will ignite the stray grains of gunpowder which may happen to have lodged on the wick.

When a heated body is suspended in the atmosphere, and freely exposed on all sides to air, it gradually parts with its excess of heat, so as to attain the temperature of the surrounding substances; but this cooling effect is produced by a variety of causes, independent of any real conducting power of the air. We have already alluded to the extreme facility with which currents are formed in air when heated substances are exposed to it; the warm air ascends, and a continual current is produced, which glides over the surface of the heated matter; thus, much heat is conveyed away by the establishment of currents, in consequence of change of density in the air. But heated bodies exposed to air also part with excess of temperature by *radiation*, a process continually going on from their surfaces, and which will presently require attention. Upon the whole, it is certain that *air is a very imperfect conductor of heat*.

REMARKS ON THE RELATIVE CONDUCTING POWERS OF BODIES. It would appear, from what has been stated, that those bodies which are the best conductors of heat, have the weakest attraction for it, and that bad conductors have the strongest attraction: the former, therefore, part with their heat more readily than the latter. Metals, which are excellent conductors, are easily heated, and as easily give out their heat. It is painful to touch metal heated to about 120° . Water scalds at 150° ; but air may be heated to 250° , or even 300° , without being painful to our organs of sensation. Sir F. Chantrey had a large oven, for drying moulds employed in bronze castings; a thermometer suspended in it generally stood at about 300° ; the workmen entered, and remained in it for some minutes without much inconvenience; and a person wholly unused to such high heats might walk into and out of it with impunity, though, to such, any attempt to remain occasioned difficult breathing, and a painful sensation about the eyes, but the skin remained parched and dry. In subjecting ourselves to atmospheres thus highly heated, it is necessary carefully to avoid the contact of any good conductor of heat: if we touch a piece of metal, it would inevitably burn; a person once inadvertently entered with his spectacles on, which, being mounted in silver, presently burned the points of contact with his face.

The relative conducting powers of metal and wood are illustrated in the application of wooden handles to metallic vessels intended to contain hot liquids; or, sometimes, where the handle is required to be of metal, a thin piece of wood or ivory is interposed between it and the body of the vessel, by which all rapid communication of heat is effectually cut off. We are familiar with the warmth, that is, with the bad conducting power of woollen clothing, eiderdown, furs, and similar articles which contain much interstitial air, and with that of other porous textures: hence also the economy of covering the exposed surfaces of engine boilers and their cylinders and pipes with felt and similar materials.

We avail ourselves of the bad conducting power of brick and stone, in the construction of furnaces intended to retain their interior heat; but where the object is to communicate heat to the surrounding air, and not

to retain it in the body of the furnace, they are made of cast or wrought iron, and the lining of brickwork is dispensed with, so that the heat may readily find its way outward.

A remarkable instance of the bad conducting power of the earthy bodies constituting volcanic ashes is cited by Lyell, (*Principles of Geology*,) in the preservation of a glacier near the summit of Etna, in consequence of its having been covered by volcanic dust, over which a current of lava afterwards flowed. He supposes that at the commencement of the eruption a deep mass of drift snow had been covered by volcanic sand showered down upon it before the descent of the lava. "A dense stratum of this fine dust," he says, "mixed with scoriæ, is well known to be an extremely bad conductor of heat, and the shepherds in the higher regions of Etna are accustomed to provide water for their flocks during summer, by strewing a layer of volcanic sand a few inches thick over the snow, which effectually prevents the heat of the sun from penetrating. Suppose the mass of snow to have been preserved from liquefaction until the lower part of the lava had consolidated, we may then readily conceive that a glacier thus protected, at the height of 10,000 feet above the level of the sea, would endure as long as the snows of Mont Blanc, unless melted by volcanic heat from below."

From volcanic and other geological phenomena, it has been inferred that the interior of the globe is in a state of intense ignition. At a depth of about fifty feet from the surface the thermometer is stationary and not affected by external changes; but at greater depths the temperature progressively increases. From such observations Cordier has surmised that the elevation of temperature would be equal to 116° for each mile of descent, and, consequently, that at a depth of about thirty miles the temperature would be about 3500° , or more than adequate to the fusion of rocks and metals. The bad conducting power of the crust of the globe is an effective obstacle to the progress of this heat towards the surface: indeed it has been demonstrated by Fourier, that even if the crust of the globe were of cast iron, myriads of years would be required for the transmission of heat from a depth of 150 miles. "The temperature of the globe now depends upon the amount of heat which it receives from the sun compared with that radiated from its surface into free space. There is reason to believe that no material change has occurred in the quantity of heat received from the sun during the historical epoch. The radiation from the surface of the earth has its limit in the temperature of the planetary space in which it moves, which Fourier deduces to be -58° , and Schwanberg, from a calculation on totally different principles, estimates at -58.6° . This low temperature appears to be attained in the long absence of the sun during a polar winter, as Captain Parry found the thermometer to fall as low as -55° at Melville Island, and Ross more lately observed a temperature so low as -60° ." (GRAHAM.)

Charcoal is among the very worst conductors of heat; and there is a well-known experiment which illustrates this, consisting in placing a tea-kettle of boiling water just taken from the fire, upon the palm of the hand: it is, of course, essential to its success that the bottom of the kettle should be well covered with soot, which is a porous form of charcoal, and effectually prevents the transmission of heat from the water within to the hand. So also when the palm of the hand is covered by a

layer of dry sand, or of fine asbestos, a red-hot iron ball may be placed upon it with impunity.

The comparative conducting power of wood and metal is also well illustrated by the following experiment: take a smooth round bar of brass, or other *metal*, about an inch in diameter, and ten or twelve in length, and stretch a strip of writing-paper tightly over a part of it, to which apply the flame of a candle or spirit-lamp, and it will be found impossible to burn or even singe the paper; for the heat passes through it to the metal, and is conducted away so rapidly, that its accumulation, or the temperature required to burn the paper, cannot be attained. If we now substitute a *wooden* bar of the same dimensions as the metallic one, stretch the paper over it, and hold it in the flame, the paper will presently singe and char, and the wood beneath will be inflamed, in consequence of its bad conducting power, which prevents the diffusion of the heat, and concentrates its effects upon the spot to which the flame is applied.

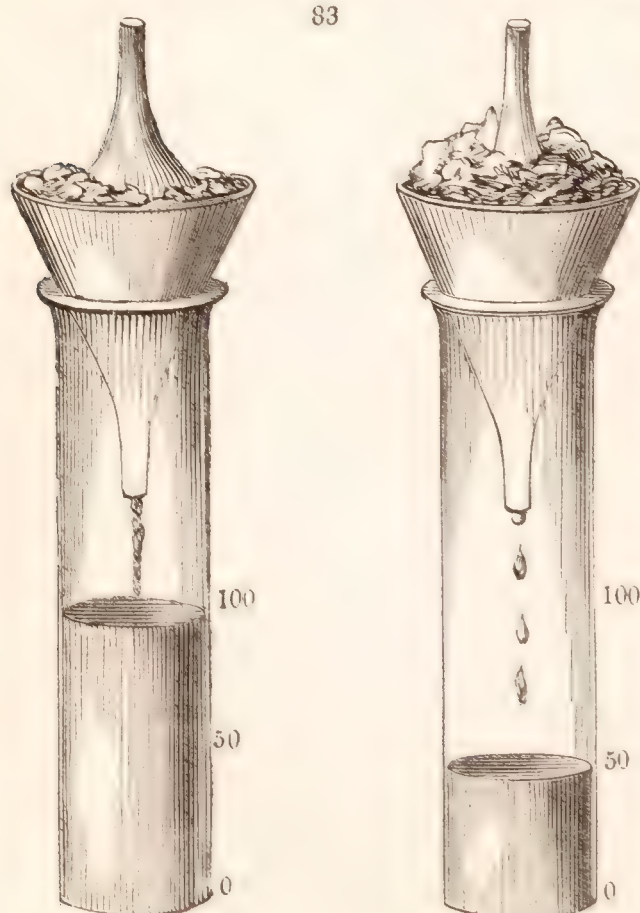
A stratum of confined air is an extremely bad conductor of heat: hence the advantage, in some instances, of double walls to furnaces, air being confined between them; and to icehouses, to exclude external heat; and of double windows to our apartments, to prevent the transmission of heat, and ingress of cold.

We have shown, that in air, the power of communicating heat is very feeble; its actual power of *abstracting* heat is also proportionably small: in the high northern latitudes, provided the air is tranquil, and there is no wind, a degree of cold may be sustained without injury, in which mercury freezes; but if, in this state of the atmosphere, *metallic* substances be touched, of the same low temperature, a sensation like that of burning is experienced, and the part becomes blistered.

Captain Parry and his associates, in their *Voyage for the Discovery of a North-west Passage*, frequently experienced a degree of atmospheric cold below the freezing of mercury. Under the date of Tuesday, the 15th of February, 1820, he says, "From four P.M., on the 14th, till half-past seven on the following morning, being an interval of fifteen hours and a half, during which time the weather was clear, and nearly calm, a thermometer fixed on a pole between the ships and the shore never rose above -54° , and was once, during that interval, namely, at six in the morning, as low as -55° . This low temperature might perhaps have continued much longer, but for a light breeze which sprung up from the northward, immediately on which the thermometer rose to -49° , and continued still to rise during the day, till at midnight, it had reached -34° . During the lowest temperature above mentioned, which was the most intense degree of cold marked by the spirit-thermometer during our stay in Winter Harbour, not the slightest inconvenience was suffered from exposure to the open air by a person well clothed, as long as the weather was perfectly calm; but in walking against a very light air or wind, a smarting sensation was experienced all over the face, accompanied by a pain in the middle of the forehead, which soon became rather severe. We amused ourselves in freezing some mercury during the continuance of the cold weather, and by beating it out on an anvil previously reduced to the temperature of the atmosphere; it did not appear to be very malleable when in this state, usually breaking after two or three blows of the hammer."

§ 7. CAPACITIES FOR HEAT. SPECIFIC HEAT.

UNDER these terms we shall consider the relation of the *temperature* of bodies, whilst in the same state or form, to the *quantity of heat* contained in them. That the thermometer is an accurate measurer of temperature has been shown by Dr. Taylor's experiment already quoted, but, as was first proved by Dr. Black in his lectures at Glasgow, in 1762, it affords no correct insight into the *absolute quantity of heat necessary to produce a given temperature*: if, for instance, a pound of olive oil and a pound of water be brought from a cold into a warm room, from a temperature of 40° to a temperature of 70° , they will, it is true, gradually acquire the same temperature; and thermometers immersed in the respective liquids will gradually rise from 40° to 70° ; but if we carefully watch the manner in which this rise of temperature is brought about, we shall find that the oil acquires the temperature of 70° more rapidly than the water; whence the inference, that the oil requires less heat to raise it from 40° to 70° than the water. Again, if we reverse the experiment, and transfer the two liquids from a warm to a cold room, it will then be observed that the oil cools more rapidly than the water: the fact being, that the quantity of heat required to raise *water* from 40° to 70° is much greater than that required to raise the *oil* a similar number of thermometric degrees, and consequently oil is more rapidly heated and cooled than a corresponding quantity of water. The following experiment proves this to be the case. A pound of *water* at 212° was surrounded, in a proper apparatus*, by ice, and the quantity of ice which was thawed by the heat given out by the water in cooling from



212° to 32° was ascertained. A similar experiment was then made with the same weight of *oil*, and it was found that, in passing through the same range of temperature, it only thawed half as much ice as the water: although, therefore, the *temperatures* of the liquids were the same at the outset and conclusion of the experiment, the quantity of heat given out by the oil was only half that given out by the water; whence we infer that *bodies, though of the same temperature, do not contain the same quantity of heat*, some requiring more, and some less heat, to raise them to a given thermometric point. The quantity of heat thus required is called the *specific heat* of the body; and if, in reference to the above statement,

* The instrument employed for this purpose was contrived by Lavoisier and Laplace, and is fully described in LAVOISIER'S *Elements of Chemistry*; they

termed it a *Calorimeter*. Its inaccuracy, resulting from the difficulty of separating the water from the ice, has been shown by Wedgwood. (*Phil. Trans.*, vol. LXXIV.)

we call the specific heat of water 100, that of oil will only be 50; or in other words, water has twice *the capacity for heat* that oil has.

This difference of specific heat in oil and water may be adequately illustrated as follows: fill two Florence flasks, one with water and the other with oil, both at 212° , and place them in large funnels upon graduated glass measures or jars (fig. 83), each flask being surrounded by bruised ice: it will be found that the quantity of water produced by the thawing of the ice surrounding the oil flask, will only be about one half that which has dropped from the water-flask, each having cooled through the same number of degrees.

It has been stated that, under proper precautions, equal quantities of the *same* fluid, at different temperatures, give the arithmetical mean, on mixture. Equal measures, for instance, of *water* at 70° , and of *water* at 130° , will give the mean temperature of 100° ; that is, the hot water loses 30° , and the cooler water gains 30° . But if equal measures of *different* fluids, as, for instance, of *water* at 70° , and of *mercury* at 130° be mixed, the resulting temperature will not be the mean, or 100° , but only 90° . Here, therefore, the mercury loses 40° , while the water only gains 20° , hence the inference, that the quantity of heat required to raise a given measure of mercury 100° , will only raise the same measure of water 50° : that is, (speaking here of equal *bulks*) the capacity of mercury for heat is only = half that of water. But the capacities of bodies for heat are most conveniently referred to equal *weights* rather than measures; and if we thus compare water with mercury, it will be found that a pound of water absorbs thirty times more heat than the same weight of mercury; viewed, therefore in this way, the capacity of water for heat is to that of mercury as 30 to 1, or as 1000 to 33, and we generally thus express the capacities of bodies for heat by a series of numbers, having reference to water as = 1000, such numbers representing their *specific heats*.

The most accurate determination of specific heats appears to be derived from the process of cooling, the time required for this purpose being directly as the specific heats of the bodies, provided they are carefully placed under similar circumstances: contained, for instance, in a polished silver vessel, in a vacuum. The following capacities were thus determined by Dulong and Petit: -

	Sp. heat.		Sp. heat.
Water	1000	Zinc	93
Sulphur.....	188	Silver	56
Glass.....	117	Mercury	33
Iron	110	Platinum.....	31
Copper	95	Lead	29

“Of all liquid or solid bodies water has much the greatest capacity for heat; hence the sea which covers so large a proportion of the globe is a great magazine of heat and has a beneficial influence in equalizing atmospheric temperature. Mercury has a small specific heat so that it is quickly heated or cooled, another property which recommends it as a liquid for the thermometer, imparting as it does, great sensibility to the instrument.” (GRAHAM.)

Dulong and Petit also have shown, as Dalton had previously anticipated, that the specific heat of bodies increases with their temperatures, so that it requires more heat to raise them a given number of degrees

when they are at a high than when at a low temperature. The specific heat of iron, for instance, at different temperatures, was as follows :

From 32° to 212°	0·1098
„ 32 to 392	0·1150
„ 32 to 572	0·1218
„ 32 to 662	0·1255

The same holds good in respect to other bodies, as shown in the following table :

	Between 32° and 212°.	Between 32° and 572°.
Mercury	0·0330	0·0350
Zinc	0·0927	0·1015
Antimony	0·0507	0·0547
Silver	0·0557	0·0611
Copper	0·0949	0·1013
Platinum	0·0335	0·0355
Glass	0·1770	0·1900

And in respect to water Regnault found that its specific heat at 40° being = 1000, at 212° it was = 1010, so that, strictly speaking, the temperature obtained by mixing equal quantities at different temperatures is not the *exact* mean, but a shade above it.

Petit and Dulong’s researches, however, render it probable that the *atoms* (or weights indicated by their equivalent numbers) of simple substances, all have the same capacities for heat; hence the specific heat of an elementary substance, multiplied into the weight of its prime equivalent, should always give the same product. (*Ann. Ch. et Ph.*, x. 403.)

The following is the table given by Gmelin in illustration of this subject: the atomic weights are those which he adopts in reference to the hydrogen unit, and they closely agree with those which I shall employ in the sequel :

	Specific heat.	Atomic weight.	Product.		Specific heat.	Atomic weight.	Product.
Oxygen	0·2361	8	1·8888	Antimony	0·0508	129	6·5532
Hydrogen	3·2936	1	3·2936	Tellurium	0·0515	64	3·2960
Nitrogen	0·2754	14	3·8556	Bismuth	0·0308	106·4	3·2771
Diamond	0·1469	6	0·8814	Zinc.....	0·0955	32·2	3·0751
Graphite	0·2019	6	1·2114	Cadmium.....	0·0567	55·8	3·1639
Charcoal	0·2009	6	1·2054	Tin	0·0562	59	3·3158
Do.	0·2415	6	1·4490	Lead	0·0314	103·8	3·2593
Do.	0·2964	6	1·7784	Iron	0·1138	27·2	3·0954
Phosphorus....	0·1887	31·4	5·9250	Cobalt	0·1070	29·6	3·1672
Sulphur	0·2026	16	3·2416	Nickel	0·1086	29·6	3·2146
Selenium	0·0837	40	3·3480	Copper.....	0·0951	31·8	3·0242
Iodine	0·0541	126	6·8166	Mercury	0·0333	101·4	3·3766
Bromine	0·1350	78·4	10·5840	Silver	0·0570	108·1	6·1617
Tungsten.....	0·0364	95	3·4580	Gold.....	0·0324	199	6·4476
Molybdenum ..	0·0722	48	3·4656	Platinum.....	0·0324	98·7	3·1979
Manganese	0·1441	27·6	3·9772	Palladium	0·0593	53·4	3·1666
Arsenic	0·0814	75·2	6·1213	Iridium	0·0368	98·7	3·6322

It will be observed that the majority of the numbers in the fourth column of this table fluctuate a little on one side or other of 32, and that where the product indicates a multiple or submultiple of 32, the atomic weight or equivalent would be required to be halved, doubled, &c., in order to assimilate it to the general law. The minor deviations may arise out of errors in the operation, or impurity of materials: the most inexplicable incongruity is in the case of carbon.

The subject of specific heat has also been elaborately investigated by

Regnault (*Ann. Ch. et Ph.*, LXXIII. 1): and in a later memoir (*Ann. Ch. et Ph.*, Nov. 1834) he has published some curious details respecting the specific heats of certain liquids isomeric with oil of turpentine; of certain metals in different mechanical conditions; and of sulphur in its various states. I have noticed some of the results under the history of the respective substances.

From the researches of Neumann (*POGGEND. Ann.*, No. 9, 1831), and of Avogadro (*Ann. Ch. et Ph.*, LV. 80, LVII. 113), it would appear that the atoms of compound bodies of similar composition also possess the same capacities for heat: this at least appears the case in regard to the following sulphates and carbonates.

	Specific heat.	Atomic weights.	Product.
Carbonate of Lime	0·2044	50	102·2
„ Baryta.....	0·1080	99	106·9
„ Iron.....	0·1819	58	105·5
„ Lead	0·0810	134	108·5
„ Zinc	0·1712	62	106·1
„ Strontia	0·1445	74	106·9
Mean			106·
Sulphate of Baryta	0·1068	117	124·9
„ Lime	0·1854	68	126·8
„ Strontia	0·1300	92	119·6
„ Lead	0·0830	152	126·1
Mean			124·1

The specific heat of gaseous bodies has been examined by De La Roche and Berard (*Ann. de Chim.*, LXXXV., or *Ann. of Philos.*, v. ii.), Haycroft, Apjohn, and others. The following tables show the results obtained by Berard:

	Equal volumes.	Equal weights.	Sp. gravity.
Air	1·0000	1·0000	1·0000
Hydrogen.....	0·9033	12·3401	0·0732
Carbonic acid	1·2583	0·8280	1·5196
Oxygen	0·9765	0·8848	1·1036
Nitrogen	1·0000	1·0318	0·9691
Nitrous oxide	1·3503	0·8878	1·5209
Olefiant gas	1·5530	1·5763	0·9885
Carbonic oxide	1·0340	1·0804	0·9569

To reduce these numbers to the standard of water, three methods were employed; from which the numbers 0·2498, 0·2697, and 0·2813 were obtained for atmospheric air. They have taken 0·2669 as the mean, to which all the above results are referred, as follows:

Water	1·0000	Nitrogen gas	0·2754
Air.....	0·2669	Nitrous oxide gas	0·2369
Hydrogen gas	3·2936	Olefiant gas	0·4207
Carbonic acid gas	0·2210	Carbonic oxide gas	0·2884
Oxygen gas	0·2361	Aqueous vapour	0·8470

An extended table of specific heats may be consulted in Dr. THOMSON'S *Outline of the Sciences of Heat and Electricity*, 2nd edit.: but there can be little doubt that many of the hitherto received results are erroneous, as will be evident from the observations of Regnault, in the paper above quoted. Some experiments on the specific heat and conducting powers of building materials, by Mr. John Hutchinson, will be found in the Proceedings of the Chemical Society (*March*, 1842).

The capacity of bodies for heat is materially affected by their *density*; whenever density is diminished, capacity for heat is increased, and *vice versâ*. Thus in regard to *solids*, if we suddenly compress a piece of metal, it becomes hot, because its capacity for heat is diminished; and, therefore, in its dense and compressed state, it contains less heat than it did before; in the process of coining, the blank piece, in sustaining the sudden and violent pressure of the coining-press, becomes suddenly warm; and a bar of red-hot iron, when subjected to great pressure, as in passing it through a powerful rolling-mill, becomes nearly white hot. Most cases of the evolution of heat by friction and percussion may be referred to the same source. A piece of soft iron, dexterously struck a few heavy blows with a hammer, becomes hot enough to inflame the sulphur of a match. A piece of Indian rubber, suddenly and forcibly drawn out, becomes warm in consequence of the extension, as may easily be perceived by applying it to the lip the moment it is stretched, that part being very susceptible of slight changes of temperature. In some of these cases, however, an altered molecular condition, or arrangement of the particles, independent of actual change of density, seems to modify their relation to sensible heat; thus heat is often indefinitely evolved by *friction*, and the specific gravity of lead is said not to be altered by hammering, yet it becomes very hot during that operation: in some cases, too, spontaneous changes of texture or aggregation in solids are attended by change of temperature: thus sugar, in changing from its vitreous to its granular or crystalline state evolves heat. Professor Graham remarked, that when melted sugar was allowed to cool to about 100° , and then whilst soft and viscid, rapidly and frequently extended and doubled up, its temperature rose in two minutes from 105° to 175° ; there can, therefore, be little doubt that the transition of vitreous into granular sugar is accompanied by a change in its relations to heat: and that glass, like transparent barley sugar, may owe some of its peculiarities to the permanent retention of heat, of which it may be deprived by keeping it long in a soft state, when it becomes granular and porcellaneous. Graham also suggests that *dimorphism* may depend upon the retention of a certain quantity of heat by the body in the one form, and not in the other. (*Elements*, p. 43.)

A change of capacity for heat, attending change of density, is also perceived in *liquids*. When sulphuric acid is mixed with water, the relative density of the mixture is suddenly and greatly increased, and it becomes boiling hot. When alcohol and water are mixed, there is also an increase of density, and heat is evolved.

In *gases* we have a convenient opportunity of observing that, as on the one hand, condensation produces heat, so, on the other, rarefaction, or diminution of density, is attended by increased capacity for heat, or, in other words, by the production of cold. Air, suddenly compressed by the piston of a syringe, evolves so much heat as to inflame combustibles exposed to it; but if we suspend a thermometer in the receiver of the air-pump, we find that, during exhaustion, the rarefaction or expansion which the air suffers, causes a diminution of several degrees of temperature; and this is one reason why the air in the higher regions is cooler than that below. As it ascends from the earth it expands; and in expanding, its capacity for heat is increased: it therefore cools itself,

as well as the surrounding bodies. The Andes, placed almost under the line, rise in the midst of burning sands; about the middle height is a pleasant and mild climate; the summits are covered with unchanging snows; and these ranges of temperature are always distinct. The hot winds from below, if they ascend, become cooled in consequence of expansion; and the cold air, if by any force of the blast it is driven downwards, is condensed and rendered warmer as it descends.

When hot steam suddenly issues, under great pressure, from a small aperture into the atmosphere, its instantaneous expansion so far cools it, that, instead of scalding the hand held in it, as is the case with ordinary steam, it scarcely feels warm. But the most remarkable case of the production of cold by the sudden expansion of a vapor is furnished by the sudden escape of carbonic acid in its passage from the liquid to the gaseous state, and its consequent solidification.—(See *Carbonic Acid*).

An analogous case is furnished by the Fountain of Hiero, as it is called, at Schemnitz, in Hungary. A part of the machinery for working these mines is a perpendicular column of water, 260 feet high, which presses upon a quantity of air enclosed in a tight reservoir: the air is consequently greatly condensed by this height of water, which is equal to between eight and nine atmospheres; and when a pipe communicating with this reservoir of condensed air is suddenly opened, it rushes out with extreme velocity, instantly expands, and in so doing it absorbs so much heat as to precipitate the moisture it contains in a shower of snow, which may be gathered on a hat held in the blast. The force of this is so great, that the workman who holds the hat is obliged to lean his back against the wall, to retain it in its position.

If the blast from an air-gun be directed upon a delicate thermometer, it sinks it a few degrees, from the cold produced by the sudden expansion of the air.

§ 8. EFFECTS OF HEAT IN CHANGING THE FORM OF BODIES. LATENT HEAT.

HAVING described the phenomena attendant upon the expansion of bodies by heat, and its propagation through liquids and gases by convection or change of density, and through solids by their conducting powers, we may now proceed to *its effects upon the forms or states of bodies*.

When *solids* are exposed to a certain degree of heat, they change their state, and are converted into *liquids*; and *liquids*, under the same circumstances, are changed into *vapors* or *elastic fluids*: these again, by the loss of heat, revert to the liquid state; and liquids, by due degrees of cold, are solidified*. *Ice, water, and steam* are familiar instances of these three states of matter, and the phenomena attendant on their production may be discussed under the heads *Liquifaction* and *Vaporization*.

* It is probable that all substances are susceptible of these changes; though, on the one hand, the temperature required for the liquifaction and evaporation of some solids is extremely high; and on the other, the temperature required for the reduction of many gases to the liquid state unattain-

ably low. Fusion is sometimes preceded by a softening of texture so as to admit of adhesion by *welding*, as in porcelain, glass, iron, and platinum: and certain solids which are very volatile rise in vapor before fusion; in order to liquify them, they require to be heated under pressure.

§ 9. LIQUIFACTION.

ONE important fact respecting the conversion of ice into water has already been mentioned, in describing the method of graduating thermometers, namely, that during the progress of thawing, the ice and the water always maintain an uniform temperature, which is equal to 32° of Fahrenheit's scale. Suppose, for instance, that we bring some pounded ice from a very cold place (say of the temperature of 0°) into a room of the temperature of 60° , the ice, of course, soon begins to liquify, and a thermometer plunged into it rises from 0° to 32° ; but there it remains *stationary* until the whole of the ice has melted: the water thus formed, then gradually rises to 60° , which is the temperature of the surrounding air. Now it is obvious, that during the whole process of thawing, heat must be entering the ice, but its effect is, not to elevate its temperature, but to melt it: the heat apparently combines with the ice, to constitute water, but it does not affect the thermometer.

To heat thus united with bodies, Dr. Black gave the name of *latent* or *combined heat*; and he instituted a number of experiments upon the subject of liquifaction and congelation, one or two of which may be here detailed: they are at once simple and satisfactory.

Two similar glass globes were filled, the one with five ounces of water, which was afterwards frozen, and the other with water cooled down to below 33° , so as just not to be frozen. That which contained the ice was allowed to remain in a warmer air, till the ice began to melt, at which time its temperature was 32° . The two vessels were then suspended in the middle of a large room without a fire, or any notable draught of air, and of the temperature of 47° . The vessels, therefore, were under similar circumstances of temperature within and without, and with similar contents, except that the one contained *ice*, and the other *water*. The progress of heating was then noted. In that which held the water, the thermometer rose in *half an hour* to 40° ; but, in the other, it took no less than *ten hours and a half* before all the ice was melted, and the contents had reached 40° . Consequently, the rate of heating was *twenty-one times slower* in the ice-vessel than in that which held the cold water; but the actual heat received by the former was obviously nearly uniform the whole time; and, therefore, it required about twenty-one times as much heat to bring ice to the state of water, and to raise it to 40° , as to raise ice-cold water to the same point. Or, to express it by another form: if the water had continued to receive as great an influx of heat as the ice during the whole twenty-one half hours, its temperature would, of course, have been raised twenty-one times as much as during the single half hour; and, as this was 7° , the whole would have been twenty-one times 7° , or 147° . The difference between the gain of temperature in the ice and the water, with equal accessions of heat, is therefore about 140° ; and thus 140° is the expression of that quantity of thermometric heat or temperature, which disappears, or is rendered latent by the separate operation of the liquifaction of ice; the actual quantities of matter in the comparison being equal. (BLACK'S *Lectures*.)

The conclusions drawn from this *slow* thawing of ice, were verified and confirmed by melting it *rapidly* by mixture with hot water. Thus, if we take any quantity of finely-pounded ice, or snow, at the temperature of

32°, and mix it with an equal weight of hot water, at a temperature of 172°, the snow melts, and the temperature of the resulting water is only 32°. Here, therefore, the water suddenly loses 140° of heat, while the temperature of the snow remains as at the outset of the experiment. So that 140° of heat have disappeared; they have combined with the snow; and their effect has been, *not to raise its thermometric temperature, but to convert it into water*. Ice, therefore, when it is converted into water, absorbs and combines with a certain proportion of *sensible* heat, and renders it *latent*. The exact number of thermometric degrees of heat which disappear during the liquifaction of ice have been somewhat differently estimated by different experimentalists. Thus, Provostaye and Regnault place it at about 142°.

From such experiments we deduce this general law—*that in all cases of liquifaction, a quantity of heat not indicated by, or sensible to, the thermometer, is absorbed or disappears; and that this heat is withdrawn from the surrounding bodies, leaving them comparatively cold.*

Accordingly, an analogous disappearance of heat is observed where the temperatures are comparatively high; spermaceti, for instance, fuses at 112°, and retains that temperature during its fusion, so long as any portion remains unmelted: when the whole is liquid, and not till then, its temperature may be elevated above the fusing-point. Again, a ladleful of lead cannot be heated red-hot till all the metal is melted; and a quantity of red-hot melted lead is instantly cooled down to its point of fusion (which is about 612°) by the addition of a piece of solid lead.

That the heat which becomes insensible, or latent, during the liquifaction of ice and other solids, *remains* in the liquid, and is not lost or destroyed, is shown by the circumstance of its being again emitted, or given out, during their congelation. If a vessel of warm water be exposed in a very cold atmosphere, the temperature rapidly sinks to the freezing-point, and then it begins slowly to congeal: if kept in the same situation, heat is of course abstracted as before; but the thermometric heat remains stationary at about 32°, till the whole is frozen, after which the temperature of the ice begins again to sink.

Perhaps the result of this experiment is more explicitly stated as follows:—If, when the thermometer is at 22°, we expose a vessel full of *water* at 52° to the open air, and beside it another vessel full of *brine*, at the same temperature, with thermometers in each, we shall find that both of them gradually lose heat, and are cooled down to 32°. After this the brine (which does not freeze till cooled down to 4°) continues to cool without interruption, and gradually reaches 22°, the temperature of the air; but the pure water remains stationary at 32°: it freezes, indeed, but very slowly; and during the whole process its temperature is 32°. Now why should one liquid refuse, all of a sudden, to give out heat, and not the other? Is it not much more probable that the water, as it freezes, gradually gives out the heat which it had absorbed during its liquifaction, and that this evolution maintains the temperature of the water at 32°, notwithstanding what it parts with to the air during the whole process? It is easily shown that water, while congealing, is constantly imparting heat to the surrounding air; for a delicate thermometer suspended above it is constantly affected by an ascending stream of air less cold than the air around. (THOMSON on *Heat*.)

The following experiment also shows that this *evolution of heat* actually takes place *during congelation*. (BLAGDEN, *Phil. Trans.*, 1798.) If, when the air is at 22° , we expose to it a covered glass of water, with a thermometer in it, the water, if kept quite still, may be gradually cooled down to 22° without freezing. It is, therefore, ten degrees below the freezing-point. If the water be now shaken, part of it instantly freezes, and the temperature of the whole rises to 32° ; so that the water acquires 10° of heat in an instant. Now, whence comes this heat? Is it not evident that it is derived from that part of the water which suddenly froze; and consequently, *that water, in the act of freezing, gives out heat?*

There are many instances of the sudden or rapid liquifaction of bodies, in which the absorption of heat, or production of cold, are more remarkable and striking than in the cases above detailed. When finely-powdered common salt, for instance, is mixed with pounded ice or snow, a *sudden liquifaction* of the solids ensues, and a proportionate *production of cold*; they immediately run down into brine, which does not freeze till reduced to nearly 0° ; and a thermometer plunged into the mixture sinks nearly to that point. We sometimes avail ourselves of this process, to remove hard trodden snow from the pavement in winter: it is soon liquified by sprinkling a little salt upon it, and the temperature of the air is seldom low enough to freeze the brine which is produced. Confectioners employ the mixture of ice and salt to freeze cream in the hot weather of summer; and the same system is conveniently resorted to whenever considerable cold is required. The production of cold by the liquifaction of metals may be well shown by melting together 207 parts of lead, 118 of tin, and 284 of bismuth; these form on cooling a brittle alloy, which when reduced to powder and dissolved in 1617 parts of mercury at the temperature of 60° , produce a liquid amalgam the temperature of which falls to 14° .

In the case of the disappearance of heat caused by the sudden formation of *liquid* brine from its *solid* constituents, the bodies being already cooled to 32° , the thermometer sinks about 30° , or to 0° . It was once supposed that this was the lowest temperature that could be artificially commanded; and hence, probably, Fahrenheit's thermometric scale sets out with it: but we now know that, by careful management, the mixture of certain materials will afford a much more intense cold. Among the most effective of these is the mixture of snow and the salt called *chloride of calcium* or *muriate of lime*: the snow should be taken in its light flocculent state, as it falls in a very cold winter's day; and the chloride in fine powder, but not deprived of all its water of crystallization, should be mixed with it in the proportion of about three parts to two: the mixture should be made in earthen vessels, previously cooled, and in the lowest atmospheric temperature we can command; the thermometer will then sink from 32° , to between 40° and 50° below 0° , a temperature at which mercury freezes. By the successive application of freezing mixtures in a proper apparatus, Walker succeeded in sinking the spirit-thermometer to -91° ; a temperature at which nearly all liquids are converted into the solid form. The following table shows some of the most useful of these freezing mixtures, and the temperatures which result from their careful application. (*Phil. Trans.*, 1795 and 1801.)

Mixtures.	Parts.	Therm. sinks.	Mixtures.	Parts.	Therm. sinks.
Sal ammoniac.....	5	From 50° to 10°	Snow	2	From -10° to -56°.
Nitre	5		Diluted sulphuric acid	1	
Water	16		Diluted nitric acid....	1	
Nitrate of ammonia	1	From 50° to 4°.	Snow or pounded ice	12	From 18° to -25°.
Water	1		Common salt	5	
Sulphate of soda	5	From 50° to 3°.	Nitrate of ammonia	5	
Diluted sulphuric acid	4		Snow	1	From -40° to -73°.
Snow	1	From 32° to 0°.	Muriate of lime.....	3	
Common salt	1		Diluted sulphuric acid	10	From -68° to -91°.
Muriate of lime	3	From 32° to -50°.	Snow	8	
Snow	2				

Whenever ice can be procured, its mixture with common salt furnishes the cheapest and most effectual freezing mixture*; but when it cannot be obtained, we often conveniently avail ourselves of the two first saline combinations in the preceding table: either the mixture of sal ammoniac and nitre or of nitrate of ammonia and water, may be used, and the salts again be obtained by evaporation. In employing them to cool a bottle of champagne, for instance, a vessel should be selected a little larger, and nearly as tall as the bottle; it should then be filled with the coldest water that can be procured, and the bottle placed in it: about four ounces of the salt in fine powder should be sprinkled upon the shoulder of the bottle, so as, gradually dissolving, to fall or run down its sides; as the salt dissolves, the bottle should be gently turned in the mixture, and kept in it till an immersed thermometer tells us that the temperature is rising, which will be in about twenty minutes or half an hour. A table of the cold produced by dissolving sulphate of soda in dilute sulphuric acid, by Professor Bischof of Bonn, will be found in Dr. Thomson's *Outline of the Sciences of Heat and Electricity*. "A very convenient process for freezing a little water without the use of ice is to drench finely powdered (crystals of) sulphate of soda with the undiluted hydrochloric acid of the shops. The salt dissolves to a greater extent in this acid than in water, and the temperature may sink from 50° to 0°. The vessel in which the mixture is made becomes covered with hoar-frost, and water in a tube immersed in the mixture is speedily frozen." (GRAHAM.)

As liquifaction is to surrounding bodies a *cooling* process, and as sudden liquifaction produces sudden cold, so solidification or congelation is to surrounding substances a *heating* process; and when it takes place suddenly, a proportionably sudden elevation of temperature is the consequence. In the experiment described in page 10, a solution of Glauber's salt is made suddenly to crystallize; and if the hand be applied to the flask, it will be found to become sensibly warm. In this case the heat evolved is chiefly referable to the water which solidifies and constitutes the water of crystallization of that portion of the salt which separates in crystals. When alcohol is added to a saturated solution of sulphate of potassa, the salt is precipitated in the solid form, and the mixture becomes warm. A strong solution of tartaric acid added in excess to a

* For the production of the most intense degree of cold, see *Solid Carbonic Acid*.

strong aqueous solution of ammonia is attended by the sudden deposition of solid bitartrate of ammonia and much heat is evolved*. When water is poured upon quick-lime, a sudden solidification of a large portion of water is effected in consequence of its attraction for the lime, which crumbles down into a dry white powder, and a great evolution of heat ensues, as we see by the steam which makes its escape in the ordinary operation of slaking lime. When water is poured upon sulphate of copper, or sulphate of magnesia, or sulphate of soda, previously deprived by heat of their water of crystallization, much heat is evolved in consequence of their resuming it: in this case also the water suddenly passes from the liquid to the solid state. A liquid alloy of sodium and potassium brought into contact with mercury, forms a hard brittle solid, with great elevation of temperature.

In some cases the same substances, in different states, may alternately produce heat and cold; thus, in the case just cited of the production of heat by sprinkling *dry* sulphate of soda with water, the salt regains and solidifies its water of crystallization; but the solution of *crystallized* sulphate of soda in water is attended by diminution of temperature: the same happens with dry and with crystallized sulphate of magnesia: so also when snow and concentrated sulphuric acid are mixed, heat is evolved; but a further addition of snow to the acid in a certain state of dilution produces cold; in the former case the effect of the affinity of the acid for water, and the resulting increase of density, preponderates; in the latter, the sudden liquifaction of the snow.

From the view, then, which we have taken of the constitution of *liquids*, it is obvious they *may be considered as combinations of solids with heat*; that, consequently, when they revert to the solid state, they give out their *heat of fluidity*, which, previously *latent*, or *insensible* to the thermometer, now becomes *sensible*, in consequence of the change of state: on the other hand, when the solids are converted into liquids, they absorb or combine with that portion of heat which is requisite to their respective fluidities. Thus, the *heat of fluidity* or *latent heat* of water is 140° , and that of the following substances in their liquid state has been determined by Irvine, namely, sulphur 144° , spermaceti 145° , lead 162° , wax 175° , zinc 493° , tin 500° , bismuth 550° . The congealing and liquifying points of different substances will be found under their individual heads, in subsequent parts of this work.

§ 10. VAPORIZATION.

LET us next examine *the effects of heat upon liquids*. When liquids are heated, they are converted with more or less facility into invisible elastic fluids, or *vapors*. When water is heated in open vessels, its temperature gradually rises, and vapor is seen to form on its surface, which increases till the thermometer rises to about 212° , which is called the *boiling-point* of water: it is then violently agitated, and gradually evaporates in the form of *steam*: but, although the source of heat is continued, the temperature of the water remains stationary, and both it, and

* In some measure connected with these subjects, and with that of specific heat, are *the thermal changes accompanying basic substitutions.*" ANDREWS. *Phil. Trans.*, 1844, p. 21. GRAHAM. *Mem. Chem. Soc.*, I. 106. II. 51.

the steam, continue at 212° . There are, therefore, in this simple operation, two leading circumstances to be attended to, namely, the degree of expansion which the water suffers by conversion into vapor; and the cause of that uniformity of temperature to which we have adverted, and which has been above noticed as furnishing one of the fixed points for thermometric graduation.

In regard to the *bulk* of steam formed by a given bulk of water, it appears, from the experiments of Gay Lussac, that a cubic foot of water is convertible into 1689 cubic feet of steam, at the temperature of 212° (the barometer standing at 29.9 inches). Watt conceived the bulk of steam to be about 1800 times that of the water; and others have far exceeded even Watt's estimate: we may, however, adopt that of Gay Lussac as the most accurate. It is generally stated, that, in round numbers, a cubic inch of water yields nearly a cubic foot of steam, at common atmospheric pressure, (the cubic foot being 1728 cubic inches.) Other liquids form different volumes of vapor; alcohol, for instance, gives 493 times its volume, ether about 212, and oil of turpentine 192, each at the temperature of 212° . It is obvious, therefore, that these vapors will differ materially in their respective densities. Steam is lighter than air, at the same temperature and pressure, in the proportion of about 10 to 16; the density of steam to that of air being as 625 to 1000. On the contrary, the vapors of alcohol, ether, and oil of turpentine are much heavier than air, the specific gravity of the first being 1.60, that of the second 2.58, and of the third 5.01, in reference to air as unity.

Steam is an invisible elastic fluid like common air, and possessed of similar mechanical properties. We are, it is true, in the habit of associating a smoky appearance with steam, because we generally observe it when it is beginning to be condensed; as when it escapes, for instance, from the spout of a tea-kettle; but, when perfectly formed, it is quite invisible, as may be shown by boiling water in a glass flask, when perfect transparency will exist in the upper part of the vessel which is filled with the hot vapor; and it only becomes visible when it escapes into the air, and suffers incipient condensation.

The same general fact, in regard to the visibility of vapor, is shown by the production of *fogs*, which are occasioned by the mixture of warm with cold air; the general depression of temperature thus produced, rendering the aqueous vapor visible, in consequence of its partial condensation. This *partial* condensation does not amount to the actual precipitation of water, or *rain*; but consists in the formation of a multitude of thin *vesicles*; and hence the appearance is often called *vesicular vapor*: it constitutes cloud, mist, and fog. *Clouds*, therefore, are formed, whenever two masses of air, of different temperatures, and each saturated with moisture, meet and mix together; but what it is that subsequently causes the condensation of the vesicular vapor, and its precipitation in the form of rain, is not exactly known*.

* "A mist or cloud consists not of solid drops, but of a multitude of very thin vesicles of water, similar to soap-bubbles. If clouds and fogs consisted of *drops*, their precipitation would be rapid; for a drop whose diameter amounted to a thousandth

part of an inch would acquire a velocity of nine or ten feet per second: whereas we see clouds hover at a small elevation for hours; and they are transported from the sea, lake, river, or marsh, from which they are raised, far into the country, or to the

Steam, as we have said, is produced by heating water to 212° under common barometrical pressure, the thermometer remaining fixed at that point, which is, therefore, called the *boiling-point* of water. *But this point, or temperature, varies with, and is immediately dependent upon, the pressure to which the surface of the water is exposed*; it is also, to a small extent, affected by the nature of the vessel containing the water. (GAY LUSSAC, *Ann. Ch. et Ph.*, vii. 307; *Quarterly Journal*, v. 361.) Thus in a glass flask the boiling-point is proportionately high and irregular, but upon throwing in a few metallic filings, pieces of wire, or other finely-divided and insoluble materials, the generation of steam is facilitated, and the boiling-point falls to its standard. Dr. Bostock observed an analogous effect in ether and alcohol. (*Ann. of Phil.*, N. S., ix. 196.) Ether, heated in a glass vessel, had its boiling-point lowered several degrees by introducing a few shavings of cedar; and alcohol of the specific gravity of $\cdot 849$ had its boiling-point reduced in the same way between 30° and 40° . If oil be present with water, the boiling-point is always raised a few degrees. (SCRIMGEOUR.)

The influence of the quality of the surface of the vessel, its cleanliness, and other circumstances, upon the boiling-point of water, and other liquids, has also been examined by F. Marcet. (*Ann. Ch. et Ph.*, 3 S., v. 449.) He found that in glass flasks the boiling-point of water varied with the quality of the glass, fluctuating between $100\cdot 3$ and 102° of the centigrade scale, and that the temperature of the produced vapor was always somewhat lower than that of the water affording it, except in vessels thinly coated with sulphur, lac, or other material having no adhesive attraction for water; in these cases only the temperature of the water and its vapor are the same, and in them the boiling-point is sensibly lower than in clean metallic vessels. If a glass vessel be perfectly cleansed by solution of potassa, or by sulphuric acid, and all chemical and mechanical impurities in that way removed, water may be raised in it without boiling, to 105° , ($= 220^{\circ}$ Fahrenheit.) In all these cases the *degree of adhesion* between the water and its containing vessel, appears to be the cause of the fluctuations in the temperature at which actual boiling ensues.

The influence of fluctuations in the barometer upon the boiling-point of water, is shown in the following table:—

Barometrical pressure, in inches of mercury.	Temperature at which water boils.
27·74	208 $^{\circ}$
28·29	209
28·84	210
29·41	211
29·80	212
30·63	213

Of course, therefore, we find considerable *diminution* in the boiling-point of water upon the summits of hills and mountains, and other elevated situations; and a very delicate thermometer indicates a lowering

tops of the mountains, where the requisite supply of moisture cannot be had in any other way. Saussure, while travelling in the Alps, happened to be enveloped in a mist which was almost stagnant. He was astonished at the size of the drops, as he thought them, and at seeing them float slowly past

him without falling to the ground. Some of them were larger than the largest peas. Catching them in his hand, he found them to be bladders, inconceivably thin. Indeed, the optical phenomena exhibited by clouds and mists show that they are of a vesicular structure.” (THOMSON.)

of the boiling-point even at the top of high buildings. The Rev. Mr. Wollaston has described the method of constructing a thermometer of extreme delicacy, applicable to these purposes. (*Phil. Trans.*, 1817.) Saussure found that, at the top of Mont Blanc, water boiled at 187° . It appears from the above table that for every inch of variation in the barometer, the boiling-point of water varies 1.76 degrees; consequently, every tenth of an inch that the barometer rises or falls, either elevates or depresses the boiling-point by about 0.176 of a degree; even the ordinary changes, therefore, in the height of the barometer will materially affect the boiling-point. In this country the *mean height* of the barometer is a little short of 30 inches: it very rarely rises as high as 31 inches, or falls below 28.5 ; so that from this cause alone, there will be a variation in the boiling-point of water of between four and five degrees.

All essential details respecting the boiling-points of individual liquids will be given under the separate heads of the substances themselves.

The boiling-points of various saline solutions are partly dependent upon the quantity and partly upon the nature of the salt dissolved, and the steam arising from them has the same temperature as that of the boiling solution. (FARADAY. GAY LUSSAC, *Ann. of Phil.*, N. S., v. 75.) The boiling-points of a number of saturated solutions of salts have been determined by T. Griffiths, of which a table is given in the *Quarterly Journal*, xviii. 90. The following are a few of the results:—

Name of salt.	Dry salt in 100 of solution.	Boiling- point.	Name of salt.	Dry salt in 100 of solution.	Boiling- point.
Acetate of soda	60	256°	Alum	52	220°
Nitrate of soda	60	246	Chlorate of potassa.....	40	218
Nitrate of potassa.....	74	238	Sulphate of copper	45	216
Sal ammoniac	50	236	Sulphate of iron.....	54	216
Common salt.....	30	224	Acetate of lead	42	215
Sulphate of magnesia	57	222	Sulphate of soda.....	31	213

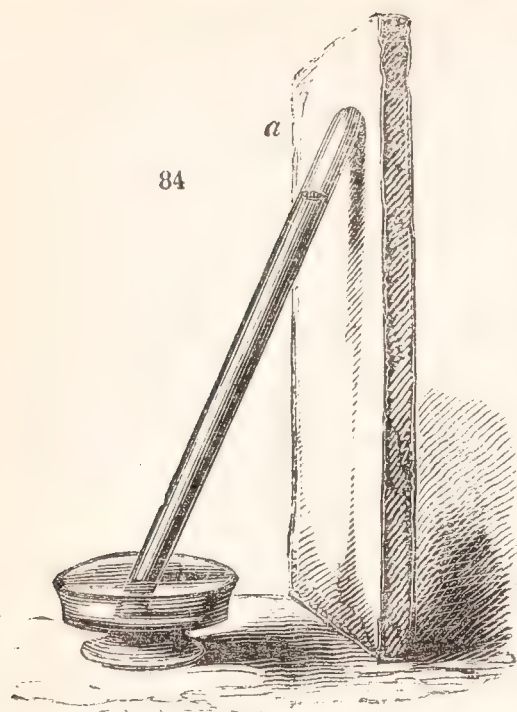
If, as has already been remarked, *pressure* be diminished by artificial methods, the temperature at which liquids boil will be proportionately lowered; and hence we often use the terms *boiling* and *ebullition* to signify the rapid conversion of water into vapor, *independent of the temperature at which it takes place*: using the term in this sense, we shall presently have occasion to point out a case of boiling at the freezing temperature.

The air-pump is a very useful instrument for showing the influence of diminished pressure upon boiling-points. If, for instance, we place a glass of water of the temperature of 90° or 100° under the receiver of the air-pump, and remove the air's pressure, the water boils violently at that temperature; and would continue so to do, but that the space in the receiver becomes filled with aqueous vapor, which, exerting its pressure upon the water, again prevents ebullition; we may, however, keep up the ebullition by continuing to abstract the vapor by the pump.

If we use liquids which, under ordinary circumstances, boil at temperatures below that of water, we find them boiling in *vacuo* at proportionately low degrees; this is the case with *ether* and with *alcohol*, which, under the above circumstances, boil at all common temperatures.

We generally apply the term *vapor* to elastic fluids which are easily reconvertible into liquids: *steam* is easily converted into *water* by lowering its temperature a few degrees; and those liquids which have low boiling-points are especially convenient for illustrating these changes;

such, for instance, as ether or alcohol; and as ether is only sparingly

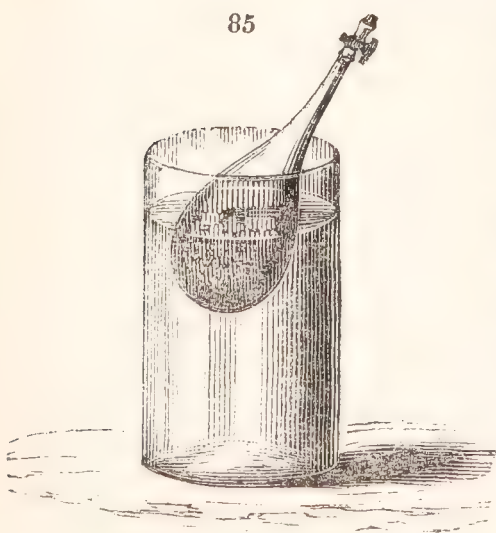


soluble in, and much lighter than water, it may be used in the following illustrative experiment. Nearly fill a glass tube about three feet long, and half an inch diameter, with water; then pour a little ether upon the surface of the water, and closing the open end of the tube carefully with the palm of the hand, invert it in a basin of water, as shown in fig. 84: the ether will rise through the water, and occupy the upper end of the tube, *a*, retaining, at common temperatures, its liquid state; but if we now pour a little hot water upon, or hold a heated iron near, the exterior of the tube, it presently causes the ether within to boil, and its vapor may thus be made to drive nearly the whole of

the water out of the tube into the basin below: the ether retains this elastic or vaporous state, so long as its temperature is sufficiently high; that is, above 100° ; but if we now cool the tube, by suffering some cold water to dribble over it, the ethereal vapor returns to its liquid state, and floats upon the water as before. At temperatures above 212° , water would be in the same predicament as ether.

With regard to the bodies usually called *gases*, they are not thus easily condensible: a few of them become liquids when considerably cooled, and several others when subjected to great pressure; but *at ordinary temperatures and pressures the gases are permanently elastic*.

The following apparently paradoxical experiment illustrates the in-



fluence of diminished pressure in facilitating ebullition. Insert a stop-cock securely into the neck of a Florence flask containing a little water, and heat it over a lamp till the water boils, and the steam escapes freely through the open stop-cock; then suddenly remove the lamp and close the cock; the water soon ceases to boil; but if the flask be now plunged into a vessel of cold water, as represented in fig. 85, ebullition instantly recommences, but it again ceases on holding the flask near the fire, or over the lamp. In this experiment the air

is driven out of the flask, and an atmosphere of steam included within it, which, upon immersion in cold water, is condensed, and a vacuum formed above the water, which, upon the principle already noticed, boils under the diminished pressure: the vacuum is kept up by the successive condensations of the portions of steam formed; but if the flask be removed from the cold medium, and especially if it be warmed, a new atmosphere of steam is formed, the pressure of which prevents ebullition.

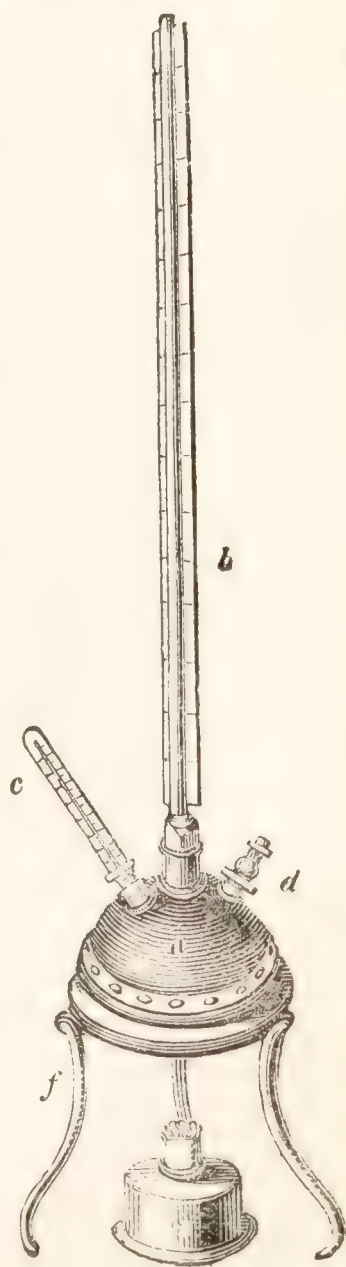
Boiling in a more or less perfect vacuum is sometimes resorted to upon a large scale in the arts; and it has been successfully applied to the refining of sugar, the syrup being thus concentrated to the granulating

point, without the risk of decomposing it. The same plan has been resorted to in the Pharmaceutical Laboratory, in the preparation of certain medicinal substances, the properties of which are easily impaired by heat. Barry has described a simple and effective apparatus for these purposes, in the *Medico-Chirurgical Transactions* (vol. x.)

If we reverse the state of things just explained, and expose liquids to *increased pressure*, we proportionately *elevate* their boiling-points. Papin contrived an instrument for this purpose, called a *digester*. It is a cylindrical copper vessel, having a lid very nicely fitted to it and secured by screws, in which is a heavily-loaded safety-valve. If such a vessel be about half filled with water, with the lid closely secured, and then put upon the fire, steam is soon formed; but having no escape, it presses upon the water, and prevents the further formation of steam till the temperature of the water rises above the boiling-point. This heat being conveyed to the steam, it now receives another portion of vapor without being condensed, and thus the *quantity* and *elasticity* of the steam are continually increasing with the temperature. Water has in this way been raised to the temperature of between 400° and 500° . Muschenbroek asserts that he raised the temperature of the water high enough to melt tin, which requires a temperature of 440° .

The powerful effects of high-pressure steam are illustrated upon a small scale by the little glass bubbles commonly called *candle or fire-crackers*; they are hermetically sealed, and contain a drop of water, which occasions them to burst with great violence, when sufficiently heated. But in speaking of the elastic force of steam, it must be recollected that it does not in itself possess greater elasticity than air, so that vessels filled with steam only, and containing no water in its liquid state, may be heated to any degree without more risk than if they only contained air.

The annexed is a form of apparatus for illustrating, within certain limits, the influence of pressure upon the temperature of steam: *a*, fig. 86, is a strong brass globe, composed of two hemispheres screwed together with flanges; a portion of quicksilver is introduced into it, and it is then about half filled with water: *b* is a barometer-tube passing through a steam-tight collar, and dipping into the quicksilver at the bottom of the globe: *c* is a thermometer graduated to about 400° , and also passing through an air-tight collar: *d* is a stop-cock, and *e* a large spirit-lamp. The whole is supported upon the brass frame and stand *f*. Upon applying heat to this vessel, the stop-cock being closed as soon as the water boils, it will be found that the temperature both of the water and of its vapor increases with the pressure, the extent of which is measured by the ascent of the mercury in the barometer-tube.



According to Southern, the temperature of steam under a pressure of two atmospheres is 250°, under that of four, 293°, and under that of eight, 344°. The results obtained by Dulong and Arago in reference to this question, are contained in the following table: they were obtained by experiment up to a pressure of twenty-five atmospheres, and at higher pressures by calculation. The first column shows the elasticity of the vapor, in reference to atmospheric pressure as = 1, and in the second column the temperature of the steam is stated in degrees of Fahrenheit's scale. (*Quarterly Journal*, N. S., vii. 119. See also Dr. Ure's table, *Phil. Trans.*, 1818.)

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
1	212	7½	336·86	19	413·96
1½	233·96	8	341·96	20	418·46
2	250·52	9	350·78	21	422·96
2½	263·84	10	358·88	22	427·28
3	275·18	11	367·34	23	431·42
3½	285·08	12	374·00	24	435·56
4	293·72	13	380·66	25	439·34
4½	301·28	14	386·94	30	457·16
5	308·84	15	392·86	35	472·73
5½	314·24	16	398·48	40	486·59
6	320·36	17	403·82	45	491·14
6½	326·26	18	408·92	50	510·60
7	331·70				

The temperature of steam is the same or nearly the same as that of the liquid producing it; hence the high temperature of steam generated under pressure: and as this elevation of temperature may be accurately regulated by the degree of pressure, *high-pressure steam* is often conveniently applied as a source of steady heat.

We are now to show, more particularly, that *the production of vapor is in all cases attended by loss of sensible heat*; and that, as in the case of *liquifaction*, heat disappears, to constitute the liquid, so, in the case of *evaporation*, heat becomes, to a much greater extent, latent in the vapor.

The fact already adverted to, that we cannot, under ordinary circumstances, raise the temperature of water above 212°, although heat continues as before to flow into it, shows that the heat must be latent in the steam, the temperature of which does not exceed that of the water which produces it; and again, when water, as in the preceding experiment with the brass globe, is heated under pressure to a temperature above its ordinary boiling-point, the moment that that pressure is removed by suddenly opening the cock, a quantity of steam rushes out, and the remaining water has its temperature lowered to 212°. The quantity of water in this case, which constitutes the lost steam, is very small, yet it carries off the whole excess of heat from that remaining in the globe.

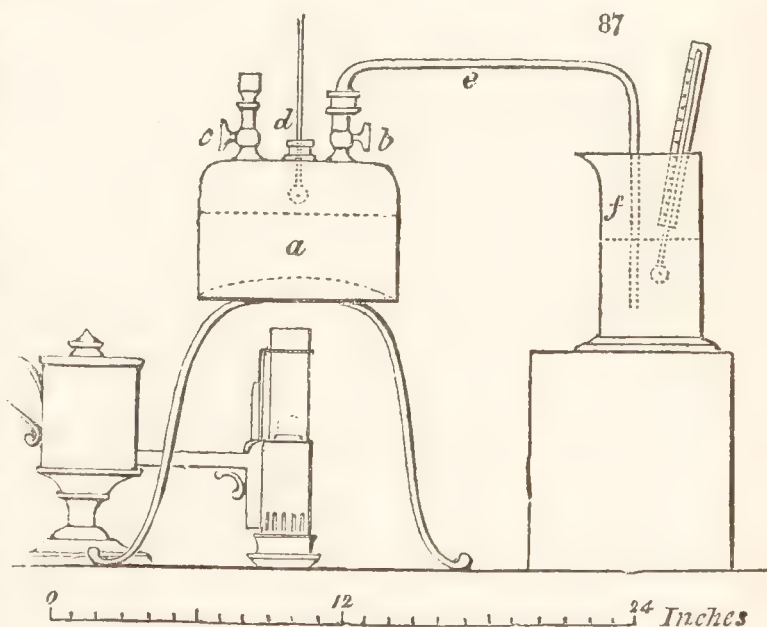
Dr. Black instituted the following experiments to determine the actual loss of heat during the conversion of water into steam. (*BLACK'S Lectures.*) He placed a flat-bottomed tin plate vessel containing a measure of water, upon a heated plate; the water was of the temperature of 50°; in four minutes it acquired a temperature of 212°, and began to boil; and in twenty minutes the whole had evaporated: the water therefore had received 162° of heat in four minutes, or 40·5° in each minute; and assuming that the heat continued to flow into the water at the same rate

during the twenty minutes required for its evaporation, he concluded that 810° (40.5×20) had become *latent* in the steam: that is to say, that the same quantity of heat which is required totally to evaporate boiling water at 212° , would be sufficient to raise the water 810° above the boiling-point, or to 1022° , if it had remained in the *liquid* state. Dr. Black verified this conclusion in another way: he heated water under pressure (in a Papin's Digester) to 400° , and then opened the valve, when part of the water suddenly rushed out in the form of steam, and the temperature of the remainder sank to 212° , so that 188° of heat disappeared, having been carried off by the steam; but only one-fifth of the water had gone off as steam; that steam, therefore, must have contained not only its own 188° , but also the 188° lost by the remaining four parts; that is, it must have contained $188^{\circ} \times 5 = 940^{\circ}$. This experiment, therefore, shows that steam is water combined with 940° of heat. From these and similar experiments on the quantity of heat which disappears during the formation of steam, the expression of its latent heat has been assumed as equal to about 1000° Fahrenheit.

On the other hand, when steam is again condensed into water, it necessarily gives out the latent heat which was essential to its state of vapor, and which, being then set *free*, will raise the temperature of adjacent bodies as much more than an equal weight of boiling water would do, as the latent heat of the steam exceeds the sensible heat of the water*.

The small boiler, represented in fig. 87, may be conveniently employed in these experiments on the latent heat of steam. (HENRY'S *Elem. Chem.*)

For this purpose the tube *e* must be screwed on the stop-cock *b*, and immersed into the glass of water *f*. The cock *c* being closed, the steam arising from the boiling water *a*, will pass into the cold water *f*, the temperature of which will be much augmented by its condensation. Ascertain the increase of temperature and of weight, and the result will show how much a given weight of water has had its temperature raised by a certain weight of condensed steam. To another quantity of



* It has sometimes been supposed from the low latent as well as sensible heat of the vapors of alcohol and ether, that they might be economically substituted for steam as sources of mechanical power, but as the cost in fuel would be proportionate

to the latent heat of equal *volumes* of their respective vapors, it will be obvious from the following statement that if alcohol and ether could be procured as cheap as water, the latter would be most economical.

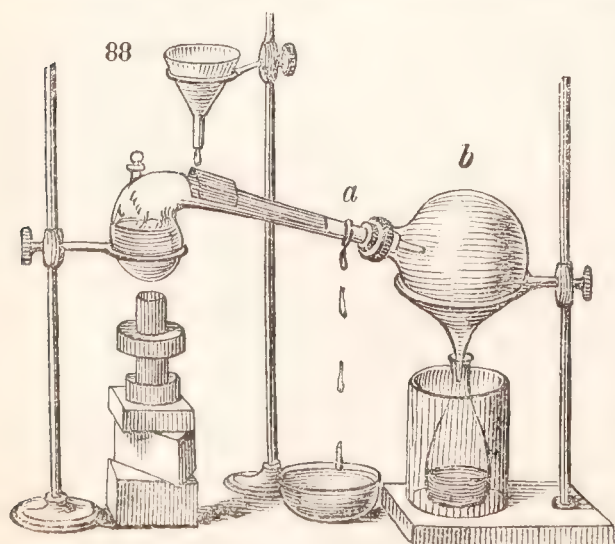
1 cubic foot of	Cubic feet of vapor.	Latent heat of equal volumes.
Water	= 1689	1000
Alcohol	= 488 : 457 :: 1689	1550
Ether	= 212 : 312 :: 1689	2500

water, of the same weight and temperature as that in the jar at the outset of the experiment, add a quantity of water at 212° , equal in weight to the condensed steam; it will be found, on comparing the resulting temperatures, that a given weight of steam has produced, by its condensation, a much greater elevation of temperature than the same quantity of boiling water. If, for instance, 100 gallons of water at 50° be mixed with 1 gallon at 212° , the temperature of the whole will be raised by about 1.5° . But, if a gallon of water be condensed from the state of *steam* into a vessel containing 100 gallons of water, the water will in that case be raised 11° . A gallon of water, therefore, condensed from steam, raises the temperature of 100 gallons of cold water 9.5° more than the addition of a gallon of boiling water; consequently, if the heat imparted to 100 gallons of water by 10 pounds of steam could be condensed in 1 gallon of water, it would raise it to 950° ; and a gallon of water converted into steam of ordinary density, contains as much heat as would bring five and a half gallons of ice-cold water to the boiling-point. The quantity of ice which is melted by steam of mean density is seven and a half times the weight of the steam.

The following is Dr. Ure's corrected table of the latent heat of steam and some other vapors. (*Phil. Trans.*, 1818, p. 389; and *Dict. of Chem.*, Art. CALORIC.)

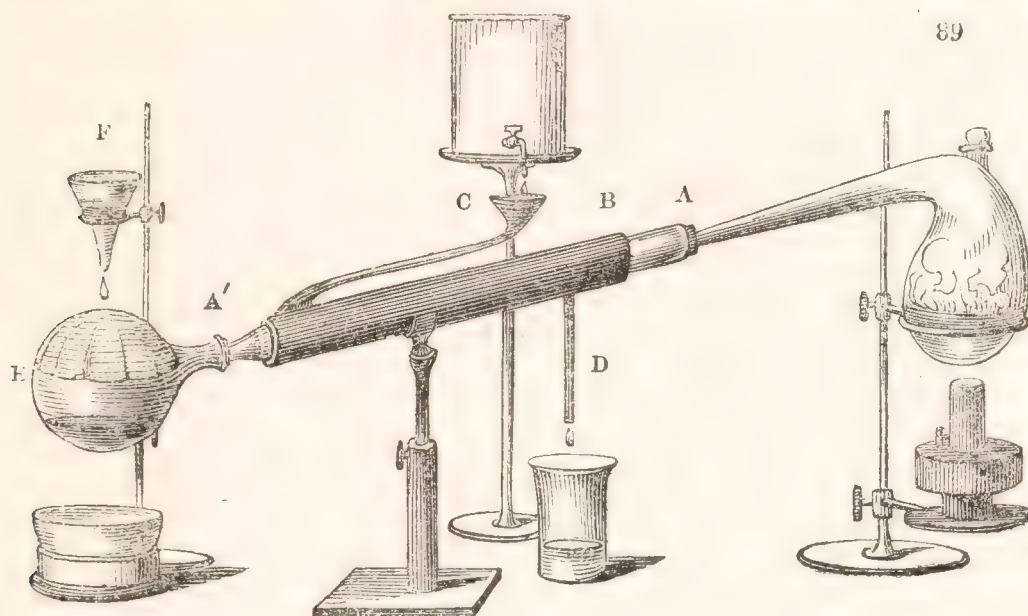
Vapor of water	1000°
„ alcohol (sp. gr. .825).....	457
„ ether (boiling-point 112°).....	313
„ oil of turpentine	184
„ petroleum	184
„ nitric acid (sp. gr. 1.494, boiling-point 165°)	550
„ aqueous ammonia (sp. gr. 0.978)	866
„ vinegar (sp. gr. 1.007)	903

In the common process of distillation, the effect of the latent heat of steam is well illustrated by what happens in the condenser, or *worm-tub* (see WATER), where a large mass of water is highly heated by the return of the vapor to the liquid state; hence the necessity of an extended condensing surface preserved at a low temperature by immersion in cold water. In distillations performed in the common glass retort and receiver, various expedients are resorted to to effect complete condensation. Sometimes the neck of the retort is covered with linen or bibulous paper, kept constantly wet by the dribbling of cold water from a



funnel or filter as in the annexed cut; a strip of tow being twisted round the tube, as at *a*, and so drawn out as to allow the drops to fall into a basin: *b* is a tubulated receiver for the further condensation of vapor, and the distilled product (or *distillate*) is ultimately collected in the receiver beneath, which if necessary may be immersed in cold water, or in a freezing mixture.

The following arrangement (known as *Liebig's Condenser*) is also effective and convenient. It consists of a slightly conical glass tube A A', eighteen or twenty inches long, and of a diameter of about one and a-half to two inches at the one end, and an inch or somewhat less at the other,



which is inclosed water-tight in a larger and shorter metal tube B, to the lower end of which is attached a funnel C, fed in any convenient way by a small current of cold water which dribbles off at the tube D. The beak of the retort is inserted at A, and the end A' terminates in the receiver E, which may itself be kept cool by the dripping funnel F. Somewhat similar contrivances are occasionally adopted on the large scale, under the name of *refrigerators*, as substitutes for the usual worm-tubs; in these a contorted pipe receives the steam to be condensed, and is surrounded by another, carrying a stream of cold water in an opposite direction.

In breweries and manufactories where large quantities of hot water are consumed, it is frequently heated by conveying steam into it, or by suffering steam pipes to traverse the vessels, or by employing double vessels. This method of warming water has also been advantageously applied to heating baths. Where a higher temperature than 212° is required, it is necessary to employ steam under adequate pressure. The heat given off by steam during its condensation, is also often applied to warming air, and is at once safe, salubrious, and economical.

Whatever may be the *density* of steam, the same weight contains the same quantity of heat, so that distillation or evaporation at low temperatures is not attended by any saving of fuel; the latent heat is increased in proportion as the sensible heat is diminished. (SHARPE, *Manchester Memoirs*, 2nd Series, ii.) "Let us imagine that in a cylinder furnished with a piston we have a certain quantity of steam, and that it is suddenly compressed by a stroke of the piston into half its bulk without being reduced to the liquid state; it would acquire double elasticity, and its temperature would be increased. If we either suppose the cylinder incapable of transmitting heat, or take the moment instantly following the compression, before any heat has had time to escape, it must be evident that the sensible and latent heat together before the compression are precisely equal to the sensible and latent heat after the compression; but in the dense steam the sensible heat is increased and the latent heat diminished by equal quantities. Reversing this imaginary experiment, if we suppose only half the cylinder to contain steam at 212° , and the piston

to be suddenly raised so as to double its volume, the density will of course be reduced to half, and its temperature will fall, but its sensible and latent heat together will remain unchanged." (DANIELL.) This fact, originally proved by Watt (THOMSON *On Heat, &c.*, p. 197), may be stated as follows:

A certain weight of steam at 212°		180° sensible heat.
condensed at 32°, gives out		950 latent heat.
		<hr/> 1130
The same weight at 250°		218 sensible.
.....		912 latent.
		<hr/> 1130
The same weight at 100°		68 sensible.
.....		1062 latent.
		<hr/> 1130

The existence of vapors of great density under high pressures and temperatures has been shown by the experiments of Cagniard de la Tour. (*Ann. Ch. et Ph.*, xxi. 127—178; *Quarterly Journal*, xv. 145.) Although pressure restrains the volatilization of a liquid, it occurred to him that there should be a limit beyond which liquids would notwithstanding be converted into vapor, provided sufficient space be allowed for its generation. A strong glass tube, two-fifths filled with alcohol, and hermetically sealed, was slowly and carefully heated; as the fluid dilated, its mobility increased, and when its volume was nearly doubled, it suddenly disappeared, and became a transparent vapor. The same results were obtained with naphtha and ether; the latter requiring less space than the former to be converted into vapor without breaking the tube, and naphtha less space than alcohol. The presence of atmospheric air in the tubes did not interfere with the results. The same experiment succeeded, through difficulty, with water, the tube containing only about one-fourth its volume. Cagniard de la Tour ascertained, by means of a mercurial gauge, the pressures of the above vapors. Alcohol, occupying in vapor a space little more than thrice its liquid volume, exerted a pressure = 119 atmospheres, and required for its production a temperature = 405°. Ether, under the same circumstances, exerted a pressure of 38 atmospheres at 320°. The temperature of the dense vapor of water was nearly that of melting zinc.

When water slowly evaporates under exposure to air, its vapor mixes with the surrounding atmosphere, and the process is usually called *spontaneous evaporation*; it takes place at all temperatures, and with a rapidity proportionate to the dryness of the air, and the velocity of the current passing over it. In manufactories, where large quantities of liquids are to be evaporated, instead of heating them in the usual way, a current of hot air is sometimes made to pass over the surface of the fluid.

As vapor slowly formed in cases of spontaneous evaporation, is similarly constituted to that produced by rapid ebullition, there being the same loss of *sensible heat* in the one case as in the other, it follows that the exhalation of humidity which is almost constantly going on from the earth's surface, must powerfully modify natural temperatures, and prevent accumulation of heat; the vapor forms mists and clouds, and when these are condensed into rain, their latent heat is again given out in the upper and cold regions. The conversion, therefore, of water into vapor, and

the condensation of vapor in the form of dew and rain, is a process of the utmost importance, as tending to equalize the temperature of the globe.

Dalton has shown that the actual quantity of vapor which can exist in any given space, entirely depends upon temperature. Thus, if some water be put into a dry flask, at 32° , very little vapor will be formed; it will contain more at 50° , and yet more at 70° . But if, being at 70° , the temperature be lowered to 32° , vapor will be condensed, and the portion retained will not exceed that originally taken up at 32° . The actual result of these experiments is the same when the flask is exhausted as when it contains air, but in the former case the evaporation is most rapid, for the air affords some mechanical resistance to the distribution of the vapor.

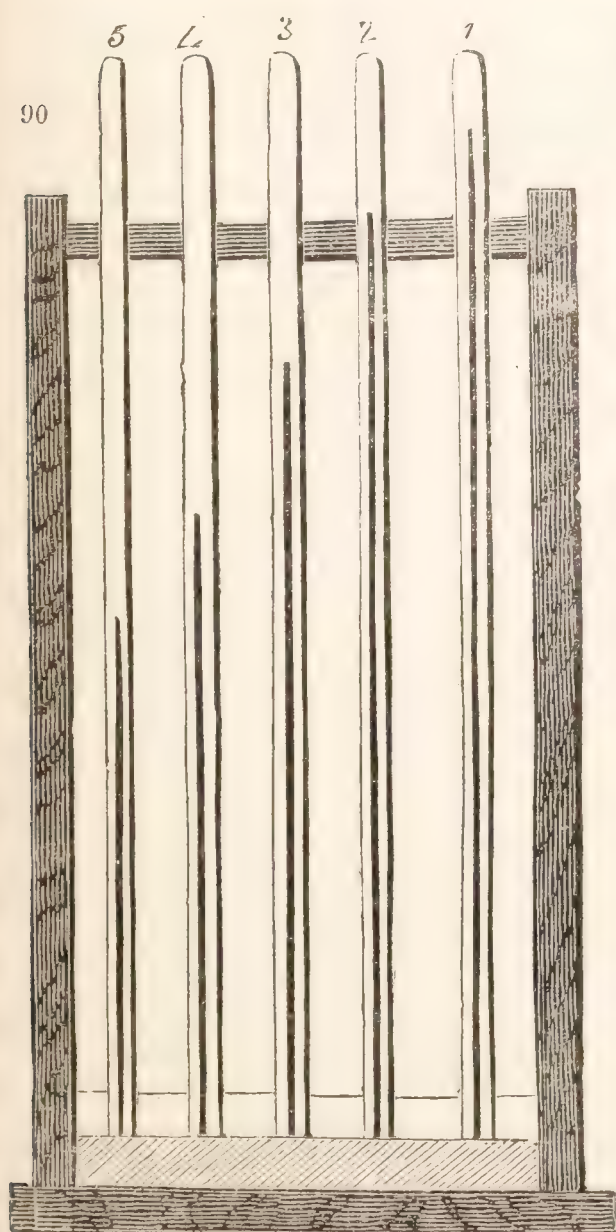
The following table shows the elastic force and the weight of aqueous vapor at different temperatures:

Temp.	Tension in inches of Mercury.	Weight of a cubic foot.	Temp.	Tension in inches of Mercury.	Weight of a cubic foot.
32°	0.216	2.53 grs.	70°	0.770	8.39 grs.
40	0.280	3.23	80	1.060	11.33
50	0.400	4.53	90	1.430	15.00
60	0.560	6.22	212	30.000	257.22

The relative volatility of bodies and the elastic force of their respective vapors may be estimated by their effects upon the column of mercury in the barometer tube. Thus, if we range five barometers side by side, one

of which may serve as a standard, and then throw up a little water into the second, alcohol into the third, ether into the fourth, and sulphuret of carbon into the fifth, each column will be depressed in proportion to the elastic force of the respective vapors. If the whole space above the mercury in each tube be equally heated, the increase of tension with increase of temperature may be measured; but if the liquids only be heated, the tension will not increase, because the respective vapors will be condensed as soon as formed. 1, represents the standard barometer; 2, the depression by the vapor of water; 3, by alcohol; 4, by ether, and 5, by sulphuret of carbon.

When liquids are exposed to the atmosphere, evaporation is proportionate to the surface exposed, and is therefore greatly accelerated by increasing the surface, as by exposing them in very shallow vessels, or suffering them to trickle over solid bodies; it is also accelerated by agitating the superincumbent air, as in the case



of a brisk wind, or by artificial means: when the air is tranquil, the vapor rests upon the surface of the water, and it is the pressure of its own vapor on the surface of a liquid, and not that of the gaseous atmosphere, which stops the process. The following table drawn up by Daniell from the experiments of Dalton, shows the force of vapor at different temperatures, and the rate of evaporation per minute from a circular surface six inches diameter; the amounts of evaporation refer to dry air; if vapor be already present, as it always is in our atmosphere, the quantity of evaporation at any given temperature will be the quantity indicated in the table, *minus* the quantity already incumbent upon the water. (DANIELL, § 196.)

Temp.	Force in inches of Mercury.	Calm. grs.	Breeze.	High Wind.
212°	30·000	120·00	154·00	189·00
85	1·235	4·92	6·49	8·04
75	0·906	3·65	4·68	5·72
65	0·657	2·62	3·37	4·12
55	0·476	1·90	2·43	2·98
45	0·340	1·36	1·75	2·13
35	0·240	0·95	1·22	1·49
25	0·170	0·67	0·86	1·05

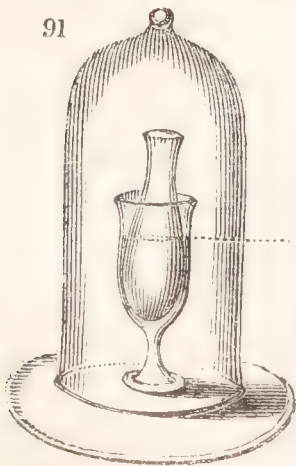
By inducing rapid evaporation, at common or low temperatures, we have it obviously in our power to produce considerable degrees of cold. If a wet cloth is spread out in a keen wind at a temperature a few degrees above freezing, the water, by its rapid evaporation, soon carries off so much heat as to freeze the remainder, making the cloth hard and stiff by the formation of ice in its pores.

There is no liquid better calculated for making experiments on the cold produced by spontaneous evaporation, than *ether*; it is extremely vaporisable at ordinary temperatures, and if we pour a little of it into the palm of the hand, and blow gently upon its surface, we observe that, as it disappears in vapor, a very sensible degree of cold is produced.

If we fold a strip of cambric round the bulb of a small thermometer and suffer ether to dribble over it from a dropping-bottle, at the same time accelerating the evaporation by blowing gently upon it with the mouth or a pair of bellows, we shall observe the mercury fall to several degrees below the freezing-point; and if we substitute for the thermometer a thin glass tube, containing a small quantity of cold water, a little dexterous management will enable us by the same means to freeze it.

This congelation of water by the evaporation of ether, furnishes, by the help of the air-pump, a very striking experiment. Provide a small thin glass flask, which fits tolerably close into a bell-shaped wine-glass, as represented by the annexed cut (fig. 91).

91

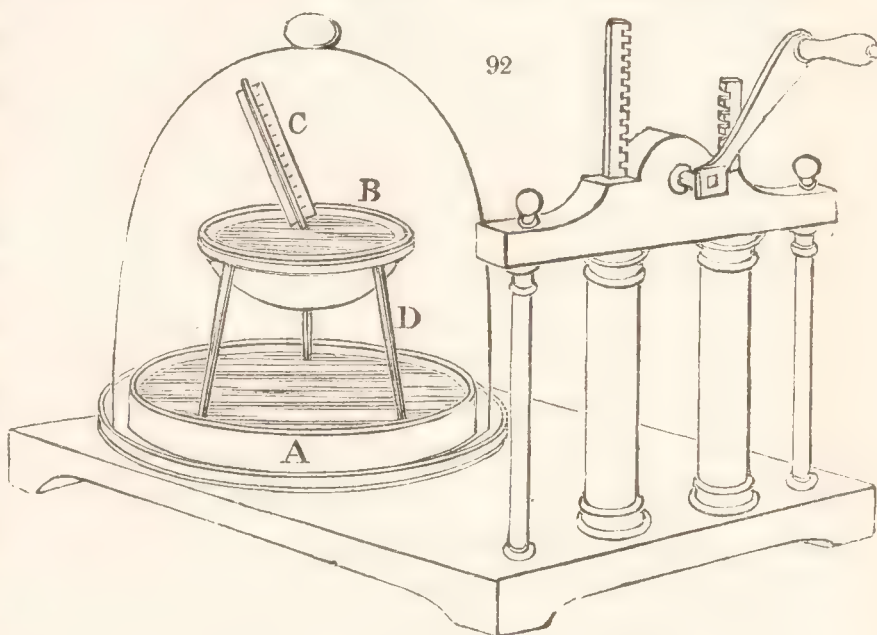


Pour a little good ether into the flask, and some cold water into the wine-glass, so that each may stand at about the level *a*, and place the whole apparatus, thus arranged under the receiver of an air-pump. During exhaustion, the ether will *boil*, that is, it will very rapidly pass off in the state of vapor. Now, the vapor of ether, like all others, requires *heat* for its formation, and this it takes from the surrounding bodies, and, among the rest, from the adjacent water, which soon *freezes* in consequence of the loss of that portion of heat which was essential to its fluidity, but which has been

carried away and pumped out in the ethereal vapor. It sometimes happens that the success of this experiment is prevented by the ether boiling over into the water and so preventing its congelation; but this may be guarded against by putting a little bit of wood or paper into the ether, which causes it to boil regularly, and prevents sudden jets of vapor.

There is an experiment yet more illustrative of the absorption and disappearance of sensible heat during evaporation, which consists in freezing water by causing it rapidly to evaporate at low temperatures; it is performed as follows:

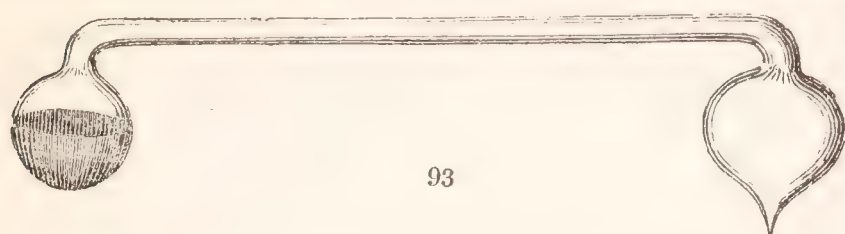
upon the plate of a good air-pump place a flat shallow glass dish, A, about half-filled with oil of vitriol, and a little above it a tin or copper basin, B, three parts filled with water, with a small thermometer, c, immersed in it (fig. 92). This basin, which should be of the shape shown in the cut, may be conveniently



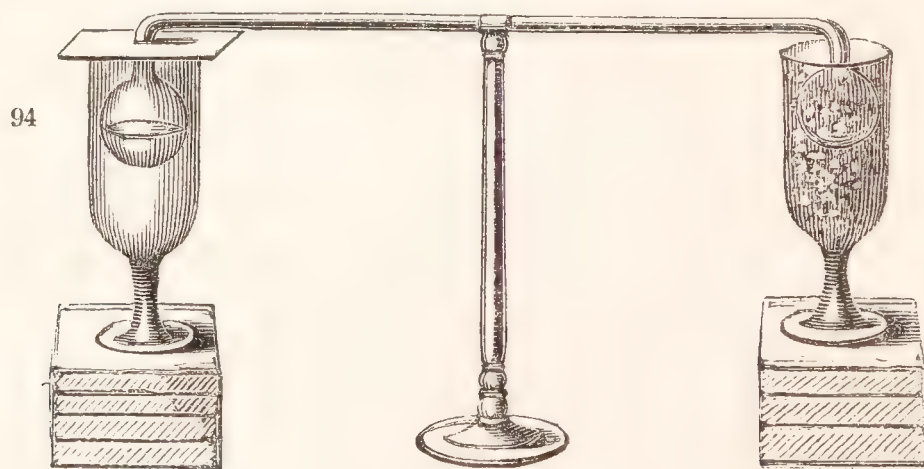
supported upon three glass legs, D, standing in the acid. Over the whole place an air-pump receiver, not larger than requisite, and proceed to withdraw the air. We first observe the escape of air from the water; the thermometer gradually sinks; the water then, in consequence of the rapidity of its evaporation, appears to boil; and if the whole apparatus is in good order, it freezes in the course of five or ten minutes. The use of the sulphuric acid is to absorb the aqueous vapor, which it does very energetically, and consequently occasions a constant fresh call upon the water for its formation. Now we have shown that *vapor cannot be produced without the absorption of heat*; and, in the case before us, the heat requisite to convert *one* part of the water into *vapor* is taken from the *other fluid portion*, which, thus losing the heat that constituted its fluidity, becomes solid, or freezes. There is another phenomenon often observable in this experiment, which is, that the temperature of the water falls several degrees below the freezing-point, before congelation takes place; but the moment that it freezes, it rises to 32° , in consequence of the escape of the residuary latent heat. Leslie, who contrived this process, proposed it as a means of procuring ice in hot climates, and suggested for the purpose, a large single air-pump, capable of exhausting six or eight receivers at a time. He has also shown, that parched oatmeal, and certain dried earthy substances, may be substituted, as absorbents, for the sulphuric acid; but they are far less effectual.

Dr. Wollaston's *cryophorus*, or ice-bearer, illustrates the same general facts, in a more simple manner than the preceding; it depends upon the same common principle, but the vacuum and the evaporation are brought about in a different way. It is a tube, having a bulb at each extremity, one of which is half filled with water, as represented in fig. 93; the interior

of the tube is perfectly deprived of air by boiling the water in one of the bulbs till a jet of pure steam issues through a small opening left at the bottom of the other, which is then sealed by fusion in the flame of a lamp; the consequence is, that the water in the other bulb is greatly disposed



to evaporate; but this evaporation can only proceed to a certain extent, because the pressure of vapor within the tube soon prevents its further progress. To get rid of this, to keep up the vacuum, and to occasion a constant demand upon the water for the fresh formation of vapor, the empty ball is plunged into a freezing mixture, which continually condenses the vapor within, and so accelerates the evaporation of the water in the other bulb, as to cause it ultimately to freeze. The success of this experiment, when it is attempted in a warm room, where there are several persons, is often frustrated by the rapid deposition of moisture, arising from the condensation of aërial vapor upon the water-bulb; an effect which may be prevented by protecting it from the free access of fresh portions of air, by immersion in a covered glass, as shown in the following sketch, fig. 94, which also represents the empty bulb surrounded by a freezing mixture of pounded ice and salt. The intermediate tube between the bulbs of the cryophorus may be of any length: about two feet is most convenient, for when longer it is very apt to be broken.



There are many cases in which we resort to accelerated evaporation, at common temperatures, as a source of cold, without, however, carrying it so far as to produce ice. The sprinkling of floors and pavements with water tends to cool them and the air by its evaporation at summer temperatures: *wine-coolers* are porous earthen vessels, which are dipped into water, and, during exposure to air, become cooled by its escape from their surfaces in the form of vapor; and in some hot climates, porous bottles are filled with water, and suspended in a current of air; the water oozes to the surface, whence it is rapidly removed by evaporation, and cold is consequently produced.

It will be obvious, from the facts now adduced, that all *vapors* may be considered as combinations of solids or liquids with heat, and Faraday's discoveries sanction us in regarding *gases* as similarly constituted; some of these are condensible by *cold*, others by *pressure*, into the liquid state: and we thus learn that they are merely the vapors of extremely volatile liquids, the boiling-points of which, under common atmospheric pressure,

are, in many instances, lower than any natural temperatures. Under great pressure these gases may be coerced into the liquid state, and, upon its removal, they instantly reassume the gaseous form, some with explosion, and some with the appearance of brisk ebullition, and the production of intense cold. (See SULPHUROUS ACID and CARBONIC ACID.)

Faraday condensed many of the gases by merely exposing them to the pressure of their own atmospheres. He put the materials for producing them into a strong glass tube, a little bent in the middle, and hermetically sealed. When necessary, heat was applied, and when the pressure within became sufficient, the liquid made its appearance in the empty end of the tube, which was artificially cooled to assist in the condensation. In these experiments much danger is incurred from the bursting of the tubes: so that the operator should protect his face by a mask, and his hands by thick gloves. He succeeded in liquifying the following gases, which, as will be seen, require various degrees of pressure for the purpose.



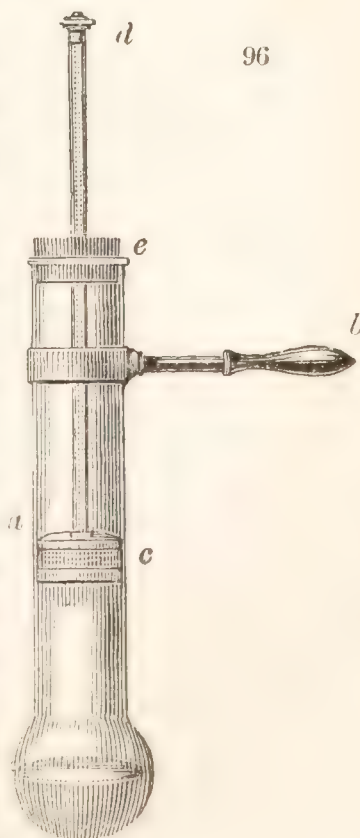
	Pressure in Atmospheres.	Fahr.		Pressure in Atmospheres.	Fahr.
Sulphurous acid	2	at 45°	Sulphuretted hydrogen	17	at 50°
Chlorine	4	„ 60	Carbonic acid	36	„ 32
Cyanogen.....	4	„ 60	Hydrochloric acid.....	40	„ 50
Ammonia.....	6 5	„ 40	Nitrous oxide	50	„ 45

By the joint influence of pressure and a very low temperature, Faraday subsequently succeeded in liquifying olefiant gas and fluosilicic acid, and in solidifying hydriodic and hydrobromic acid gases, oxide of chlorine, and nitrous oxide. (*Phil. Trans.*, 1823 and 1845.)

§ 11. THEORY OF THE STEAM-ENGINE.

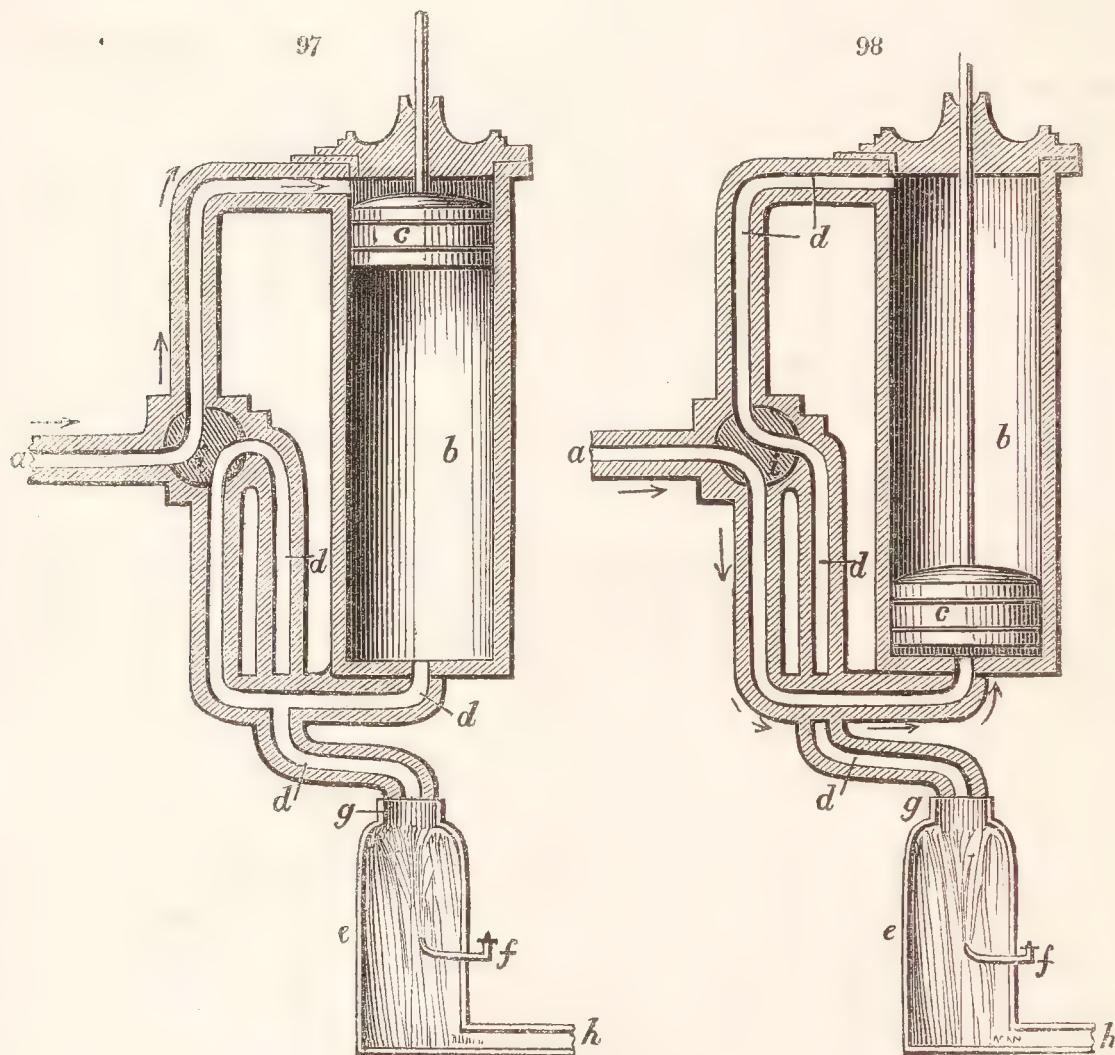
So many of the phenomena attendant on evaporation and liquifaction are illustrated by the action and principles of the *steam-engine*, that it may be worth while to refer to the construction and operation of that machine as elucidating several points already adverted to.

The action of the steam-engine depends principally upon the two leading properties of steam which have been dwelt upon—namely, *its expansive force, and its easy condensation*. To take the most simple view of these as moving powers, let *a*, fig. 96, represent a glass tube with a bulb at its lower end. It is held by a ring and handle *b*, and contains a piston *c*, which, as well as its rod, is perforated, and may be opened or closed by the screw at top *d*: it is kept central by passing through a slice of cork at *e*. When used, a little water is poured into the bulb, and carefully heated over a spirit-lamp; the aperture in the piston-rod being open, the air is thus expelled, and when steam freely follows it, the screw may be closed, when, on applying cold to the bulb, the included steam is condensed, and a vacuum formed, which causes the descent of the piston, in consequence of the air pressing upon it from above. On again holding the bulb over the lamp, steam is



reproduced, and the piston again forced up; and these alternate motions may be repeatedly performed by the alternate applications of heat and cold. This instrument gives a tolerably correct notion of the application of steam in the old engines, where it was employed conjointly with the air's pressure as a moving power.

In the most perfect construction of Watt's engine, steam is exclusively employed both for elevating and depressing the piston; and the following diagrams and description may perhaps enable the reader to understand the very ingenious method in which it is thus applied:—(see figs. 97 and 98.)



a is the *steam-pipe* issuing from the boiler, and so contrived as alternately to deliver steam into the *cylinder b*, above and below the piston *c*.

b is the main *cylinder* of the engine.

c is the *piston*, with the *piston-rod* passing through an air-tight collar at the top of the cylinder, which is commonly called the *stuffing-box*.

d is the *eduction-pipe*, by which the steam, having performed its duty in the cylinder, makes its escape into the *condenser*.

e is the *condenser*, immersed up to the level *g*, in a cistern of cold water.

f, the *injection-cock*, by which a small jet of cold water is admitted into the condenser.

h, a pipe communicating with a pump called the *air-pump*, by which the condensed steam and injection water are continually pumped out of the condenser: it also pumps out the air, and keeps a constant vacuum in the cylinder and condenser.

i represents the moveable plug of a cock which has two passages, and which opens alternate communications with the steam-pipe and the eduction-pipe. In fig. 97 this plug is shown in the position which admits the steam to pass into the cylinder *above* the piston: in fig. 98, the plug has shifted its position, and now admits the steam to pass into the cylinder *below* the piston: in the former case the condenser is open to the space below the piston; in the latter, to the space above the piston.

Let us now suppose a vacuum to exist in the cylinder *b*; the steam passes through the pipe *a*, in the direction of the arrows (fig. 97), and

entering the cylinder *above* the piston, immediately forces it *downwards*. The piston having reached the bottom of the cylinder, the plug of the cock *i* shifts its position, and is now as represented in fig. 98: the steam enters as before at *a*, and passes in the direction of the arrows to the *bottom* cylinder, so as to *elevate* the piston. It is obvious that this action could not take place unless the steam, by which it had previously been depressed, were removed; this therefore makes its escape by the *eduction-pipe d*, (fig. 98), and passes into the *condenser e*, where it reverts to the state of water, which is got rid of by the *air-pump* through the pipe *h* (fig. 97). The piston being now in the position represented in fig. 97, and the plug having again shifted its position, the steam enters *above* the piston as before, while the space *under* the piston has now a free communication with the condenser by the eduction-pipe *d*; so that the steam, which had first been active in raising the piston, is not in the way of its depression. I have here represented and described what may, perhaps, be called the simplest form of this engine, in order to render its *principle* intelligible. Instead of the four-way plug *i*, sliders or sliding-valves are generally used, as being less liable to wear, and more easily kept air-tight; but in all cases the same alternate communication with the boiler and with the condenser is effected.

§ 12. RADIANT MATTER. REFLECTION AND REFRACTION OF LIGHT.

OF the substances belonging to our globe, some are of so subtile a nature as to require minute and delicate investigation to demonstrate their existence; they can neither be confined nor submitted to the usual modes of examination, and are known only in their states of motion, as acting upon our senses, or as producing certain changes in the more gross forms of matter. They have been included under the general term of RADIANT, IMPONDERABLE, or ETHEREAL MATTER, which, as it produces different phenomena, must be considered as differing either in its nature or affections. Respecting the nature of these phenomena, two opinions have been entertained, and each ably supported. It has been supposed by Huygens, Euler, and Descartes, that they arise from vibrations of a rare elastic medium which fills space; while Newton has considered them as resulting from emanations of particles of matter. The former opinion has been ably advocated by Dr. Young, who has selected from Newton many passages favorable to the undulatory theory, and has shown that it explains phenomena not easily consistent with the theory of radiating particles. (YOUNG'S *Nat. Phil.*, ii. 631. See also FRESNEL'S Exposition of the Undulatory Theory in the first volumes of the *Quarterly Journal*, N. S.)

It may suffice here merely to advert to these opinions, without touching upon the reasoning by which they are respectively supported, and which has no immediate connexion with chemical science: there are, however, certain affections and effects of light, and of the heat that radiates from the sun, and from terrestrial bodies, which form an important part of chemical philosophy, and constitute one of the principal links by which it is connected with physical inquiries.

The phenomena of vision are produced either by bodies inherently luminous, such as the sun, the fixed stars, and incandescent substances; or they are referable to the reflection of light from the surfaces of bodies. It is thus that the objects around us are visible by reflecting the sun's

rays in the day-time, but become lost in obscurity when that luminary sinks beneath the horizon. The manner in which the eye is affected by luminous bodies, shows that light is transmitted in *right lines*, and every right line drawn from a luminous body to the eye is termed a *ray of light*; and, as a congeries of rays possesses the same properties as the single ray, the same abstract term is frequently employed to designate the congeries, which is also called a *pencil* of rays.

MOTION OF LIGHT. The discoveries of Roemer, (*Phil. Trans.*, vol. xii.,) and of Bradley, (*Phil. Trans.*, vol. xxxv. and xlv.,) have shown that *the motion of light is progressive*, and that it is about eight minutes and thirteen seconds in passing from the sun to the earth, so that it may be considered as moving at the rate of 192,000 miles in a second; in the language of Herschel, (*Discourse on the Study of Natural Philosophy*, p. 23,) it performs the tour of the world “in about the same time that it requires to wink with our eyelids, and in much less that a swift runner occupies in taking a single stride.”

We get some notion of *the velocity of light* by comparing it with the progress of *sound*, which moves at the rate of about 1000 feet in a second, or 760 miles in an hour; yet, its comparatively tardy progress is recognised, in observing the time that elapses between the flash and the report of a gun fired at a distance; the latter reaching the ear some time after the former comes to the eye; a period of nearly five seconds elapses when the gun is only a mile off, and we are thus enabled with some degree of accuracy to calculate the distance of luminous phenomena attended by sound: the varying time that elapses between seeing a flash of lightning and hearing the thunder is another familiar instance, and from it we infer the distance and course of the electric discharge.

Although, therefore, the sun is so far distant from the earth, that a cannon-ball, proceeding with its greatest speed, would be twenty years in reaching it*, and, that although almost a million times larger than the earth, its magnitude, as viewed from the earth, scarcely exceeds that of the moon, which is not much more than one-fourth the diameter of our globe, (the former 2160; the latter 8400 miles; the diameter of the sun being 882,000 miles,) yet such is the velocity of light, that a flash of it from that luminary would be seen in little more than eight minutes after its emission; whereas, the sound evolved at the same time (supposing a medium like air capable of conveying sound between the sun and the earth, and the distance 95 millions of miles) would not reach us in less than 14 years and 87 days.

From these considerations it is evident that certain astronomical phenomena are not visible upon the earth, till a certain time after their occurrence; and it was this observation, as applied to the eclipses of Jupiter's satellites, that formed one of the data upon which the velocity of light was determined, and which led to the discovery of its progressive motion. The earth's motion, in reference to that of light, gives rise to the phenomena of *aberration*, for the earth will have moved a certain distance in

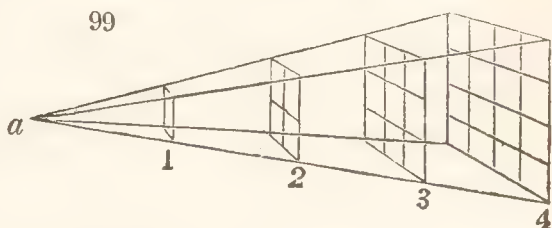
* “The earth, moving at the rate of nineteen miles in a second, would take two months to pass through a distance which a ray of light would dart over in eight minutes. The subsequent discovery of the aberration of light confirmed this astonishing result.”—MRS. SOMERVILLE.

her orbit during the time that a ray of light, which renders a star visible, is passing from it to the observer ; consequently, the *apparent* differs from the *real* place of a star.

Some bodies intercept light, or are *opaque* ; others allow its transmission, or are *transparent* ; and there are gradations from perfect opacity to nearly perfect transparency, as we see in *semitransparent* or *translucent* bodies.

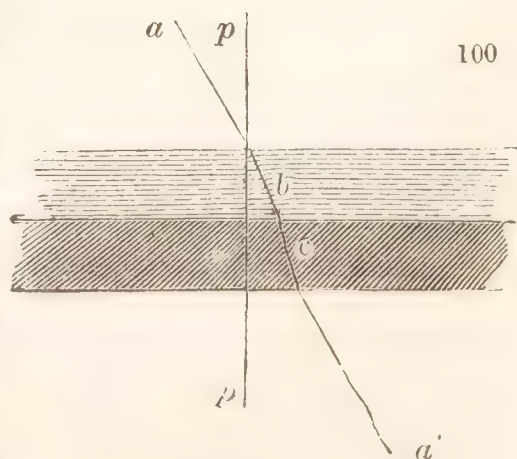
But although we are in the habit of using the terms *perfect transparency* and *perfect opacity*, such states do not in fact exist : for the air, glass, water, and similar media, all arrest or absorb certain portions of light ; whence it is inferred that perfect darkness may prevail in the depths of the ocean ; and, on the other hand, that the most opaque substances, if sufficiently attenuated or extended, would transmit light, as is the case with gold, and with exceeding thin laminæ of some other metals.

The transmission of light in right lines is evident from the phenomena of the shadows of opaque bodies, and its intensity diminishes as the squares of the distance. Thus, if an opaque screen one foot square be placed at a certain distance from a light at *a*, it will exactly shadow a second screen, two feet square, at double the distance ; a screen three feet square at thrice the distance, and one of four feet square at four times the distance ; that is, the light concentrated upon the first screen would extend itself over four times the space, if suffered to fall upon the second, over nine times upon the third, and over sixteen times upon the fourth.



REFRACTION OF LIGHT. When a ray of light passes through the same medium, or when it passes perpendicularly from one transparent medium into another, it continues to move without changing its direction ; but when it passes *obliquely* from one medium into another of a different density, it is thrown more or less out of its old direction, and is said to be *refracted*. The refraction is *towards* the perpendicular when the ray passes into a denser medium, and *from* the perpendicular when it passes into a rarer medium. The medium in which the rays of light are caused to approach nearest to the line perpendicular to its surface, is said to have the greatest refractive density.

In the following diagram, fig. 100, *a* represents the oblique ray passing through *air*, and entering *water* at *b*, and *glass* at *c*, and emerging into the *air* at *a'* ; *p. p.* is a perpendicular line, towards which the ray is refracted, in the medium *b*, and to a still greater extent in the denser medium *c* ; but on again emerging into air at *a'*, it turns from the perpendicular, and resumes its former line of passage.

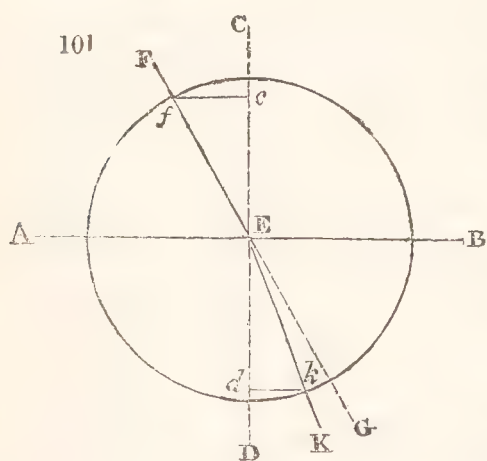


We accordingly find that when the ray *a* traverses one and the same medium, differing in different parts in its *density*, it will suffer a deflection in various parts of its course proportionate to the density of the medium. We know that the density of the atmosphere is greatest at the earth's surface, and that it decreases as we ascend, gra-

dually becoming more and more attenuated; hence, supposing the temperature uniform, the refractive power of the atmosphere would be greatest at the earth's surface, and gradually diminish as we recede from it; a ray of light, therefore, passing obliquely from a celestial object and falling upon this variable atmosphere, would be gradually more and more bent in its passage through it, and move in a curved line, exactly as if the atmosphere consisted of an infinite number of layers, gradually increasing in density from above downwards.

It is this deflection, or refraction of light, that causes bodies to appear bent or distorted when viewed through transparent media, such as water or glass: thus a stick, plunged into water, looks as if it were bent or broken; and for the same reason, a piece of money, placed at the bottom of a basin, appears to be raised when water is poured upon it; so that if, in the first instance, the eye be so placed, in reference to the edge of the basin, as just to see the further edge of the coin, on pouring water into it, the whole of it will be visible: by spirit of wine it will appear to be still more raised than by water; and by oil more than by spirit. In none of these cases, however, is the object thrown aside to the right or left; the plane in which the eye and the object are contained, is an upright or vertical plane, and in ordinary refraction the ray never quits this plane.

In the annexed diagram, if the line AB represent the surface of a refracting medium, such, for instance, as water, and F a ray of light falling obliquely upon its surface at E , the portion of that ray which enters the medium will not continue to pursue its former direction, namely, that of EG , but will (as already stated in reference to the description of the preceding diagram, fig. 100) be bent or refracted towards the perpendicular

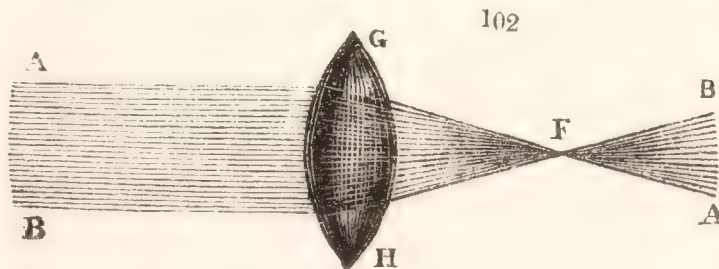


line CD : FEC , therefore, will represent *the angle of incidence*, and DEK *the angle of refraction*. If we now draw the lines fe and dk , fe will be the sine of the angle of incidence, and dk the sine of the angle of refraction, and these sines will bear a constant ratio to each other for each refracting substance, dk being to fe as unity is to the refracting power of the medium; or in the case of *water* as 1 to 1.336. This latter number, *the index of refraction* of the me-

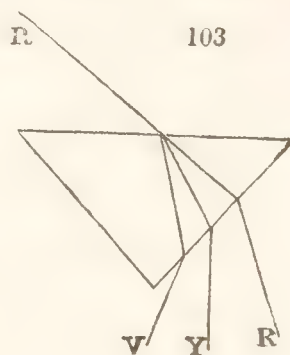
diu AB , is in all cases found by dividing the sine fe by the sine dk . The index of refraction of chromate of lead is as high as 2.974, while that of air (a vacuum being = 1), is 1.00029; and every intermediate degree of difference exists between these extremes.

We now see why, in viewing objects through refracting media, they are more or less thrown out of their real places; and how it is that in consequence of atmospheric refraction, the sun and stars are visible before they actually emerge from, and after they have sunk beneath, the horizon; and as, on the one hand, in consequence of the progressive motion of light, and the great distance of the objects, celestial phenomena are not seen till an appreciable time after their actual occurrence; so, on the other, in consequence of refraction by the atmosphere, they are not seen in their real places; with the exception, indeed, of stars in the zenith.

The ultimate direction of a refracted ray of light is influenced by the relative position of the surface of the refractor, both at its point of entrance and exit. Thus by refraction at convex surfaces the rays may be converged to a focus, as by a common lens, the refraction in these cases taking place, as if each ray fell upon a plane surface tangent to the curve at the point of incidence. Thus, if GH (fig. 102) represent a glass lens, the convex surfaces of which are segments of similar spheres, the rays AB in passing through it will be refracted at both surfaces, and on emerging from the glass will meet at the focus F , and crossing each other pass on to BA .



As it is at the surfaces of bodies that the deflecting power acts, they may be so adjusted as to double the deviation of the emerging ray: the ray R , for instance, falling obliquely upon the surface of a prism is refracted towards the perpendicular, and on again emerging is further bent in the direction Y : it is also split into different portions, of which v and R are the extremes. This phenomenon, as connected with the decomposition of light, will be noticed further on.



But there is a *limit of the angle of refraction* at which the ray, instead of emerging from the medium, is entirely reflected within it, and the brilliancy of the light thus reflected is very remarkable: it may be well shown by filling a glass with water and holding it up so that the surface of the fluid may be seen obliquely from beneath: it appears like highly-burnished silver, and objects held above it will not be visible provided the eye be kept within the limiting angle.

The density of bodies is not the only circumstance that affects their refractive power, it also depends upon their chemical nature; and, generally speaking, those substances have the greatest refractive power which are combustible, or which contain an inflammable basis. Nor is the refractive power of *compounds* the mean deduced from that of their components; which, however, it generally is, in mere *mixtures*. Hydrogen, sulphur, phosphorus, diamond, bees'-wax, amber, oil of turpentine, camphor, linseed oil, and olive oil, have refractive powers from two to seven times greater in respect to their density than those of most other substances. Newton, observing the high refractive power of the diamond, inferred that it was "an unctuous substance coagulated," long before its combustibility and real nature were known. This law seemed at one time to be opposed by an observation of Dr. Wollaston respecting *phosphorus*, which led him to ascribe to it a low refractive power; but Sir D. Brewster, confiding in the truth of the generalization, found, by forming it into prisms and lenses, that its refractive power was double that of the diamond when compared with its density.

The following is a table of the refractive powers of several gases and vapors, (DULONG, *Bulletin Philomat.*, 1825, *Ann. Ch. et Ph.*, xxxi. 154.) It shews that the refractive power of compound gases sometimes falls short of the mean calculated from their components. Column A indicates the gas or vapor; B its refractive power in reference to air as $= 1$;

c the refractive power deduced as the mean of the components; d the specific gravity: e the specific refractive power given by dividing the refractive power by the specific gravity.

A	B	C	D	E
Air	1.000	1.0000	
Oxygen	0.924	1.1093	0.83
Hydrogen	0.470	0.0693	6.79
Chlorine	2.623	2.4543	1.06
Nitrogen	1.020	0.9706	1.05
Carbonic oxide	1.157	0.9706	1.21
Carbonic acid	1.526	1.619	1.5252	1.00
Sulphurous acid	2.260	2.2185	1.02
Sulphuretted hydrogen	2.187	1.1786	1.85
Sulphuret of carbon vapor	5.179	2.6345	1.97
Hydrochloric acid	1.527	1.547	1.2618	1.21
Phosgene gas	3.936	3.784	3.4219	1.15
Nitrous oxide	1.710	1.482	1.5252	1.12
Nitric oxide	1.030	0.972	1.0399	0.99
Ammonia	1.309	1.216	0.5893	2.22
Olefiant gas	2.302	0.9706	2.36
Marsh gas	1.504	0.5546	2.71
Cyanogen	2.332	1.8026	1.57
Hydrocyanic vapor	1.531	1.651	0.9359	1.63
Alcohol vapor	2.220	1.5946	1.39
Ether vapor	5.280	2.5652	2.05
Hydrochloric ether vapor	3.720	3.829	2.2322	1.67

From these data Dulong concludes that in acid compounds the refractive power is below the mean of the components, but above it in alkaline and neutral combinations. Assuming that the refractive power of the elements is directly as their density and combustibility, the latter should be found by dividing the refractive power by the specific gravity: the quotients in column E are upon the whole consistent with this view; hydrogen has the greatest refractive power, and oxygen (the most opposed to the combustibles) the least: so also in regard to the other numbers, except that the refractive power of sulphuret of carbon ought to be below that of sulphuretted hydrogen, inasmuch as the former contains 2 atoms of the less combustible sulphur to 1 atom of carbon, while the latter contains 1 atom of sulphur and 1 of hydrogen; so also should nitrous oxide stand below nitrogen, since nitrogen by combining with oxygen ought to lose in refractive power. (L. GMELIN, *Handbuch*, i. 89.)

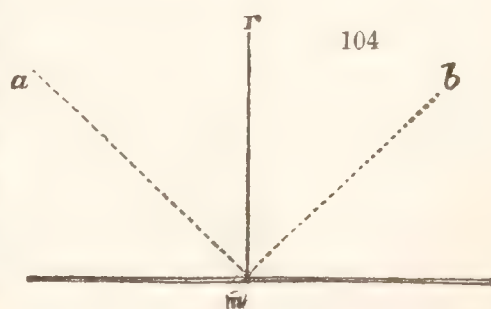
The following table gives the indices of refraction for the greater part of the substances hitherto examined. (BREWSTER. *Optics. Cabinet Cycloped.*, p. 370.) They are referred to a vacuum as = 1.

	Index of Refraction.		Index of Refraction.
Chromate of lead	2.974	Sapphire	1.794
Realgar	2.549	Ruby	1.779
Octohedrite	2.500	Spinel	1.764
Diamond	2.439	Cinnamon stone	1.759
Nitrite of lead	2.322	Sulphuret of carbon	1.768
Blende	2.260	Oil of cassia	1.641
Phosphorus	2.224	Balsam of tolu	1.628
Sulphur	2.148	Guaiacum	1.619
Glass (oxide of lead 3, flint 1) ...	2.028	Oil of aniseed	1.601
Zircon	1.961	Quartz	1.548
Glass (oxide of lead 2, flint 1) ...	1.830	Rock salt	1.557
Garnet	1.815	Melted sugar	1.554

	Index of Refraction.		Index of Refraction.
Canada balsam	1·549	Alum	1·457
Amber	1·547	Fluor spar	1·434
Plate glass..... from 1·514 to	1·542	Sulphuric acid	1·434
Crown glass	1·525 „ 1·534	Nitric acid	1·410
Oil of cloves.....	1·535	Hydrochloric acid.....	1·410
Balsam of capivi	1·528	Alcohol	1·372
Gum arabic	1·502	Cryolite	1·349
Oil of beechnut	1·500	Water	1·336
Castor oil	1·490	Ice	1·309
Cajeput oil.....	1·483	Fluids in minerals.....	1·131
Oil of turpentine	1·475	Tabasheer	1·111
Oil of olives	1·470		
Air	1·000294	Carbonic acid gas	1·000449
Vapor of sulphuret of carbon	1·001530	Carburetted hydrogen gas ...	1·000443
Phosgene gas	1·001159	Ammoniacal gas	1·000385
Cyanogen	1·000834	Carbonic oxide gas	1·000340
Chlorine	1·000772	Nitrous gas	1·000303
Olefiant gas	1·000678	Nitrogen	1·000300
Sulphurous acid gas	1·000665	Atmospheric air	1·000294
Sulphuretted hydrogen gas ...	1·000644	Oxygen	1·000272
Nitrous oxide gas	1·000503	Hydrogen	1·000138
Hydrocyanic acid vapor	1·000451	Vacuum.....	1·000000
Hydrochloric acid gas	1·000449		

Dr. Wollaston invented an apparatus in which, by means of a rectangular prism of flint-glass, the index of refraction of substances may be read off at once by a vernier, the three sides of a moveable triangle performing the operation of reduction in a very compendious manner. As the chemical constitution of bodies may, in some instances, be inferred from their refractive power, he suggested the application of such an instrument for discovering the purity of essential oils: in oil of cloves, for instance, he found a wide difference in refractive power, that of the genuine oil being as high as 1·535, while other samples did not exceed 1·498, and were probably adulterated. (*Phil. Trans.*, 1802.) In thus employing this test, however, it must be recollected, that the refractive power of the genuine oil may vary. Some improvements of the instrument have been suggested by Cooper. (*Mem. Chem. Soc.*, i. 234.)

REFLECTION OF LIGHT. When the rays of light arrive at the surfaces of bodies, a part of them, and sometimes nearly the whole, is thrown back, or *reflected*, and the more obliquely the light falls upon the surface, the greater in general is the reflected portion. In these cases the angle of reflection is equal to the angle of incidence. Suppose a ray of light to impinge *perpendicularly* upon the surface of a mirror, as at *r m*, but one ray is seen, for the ray of incidence and that of reflection are both in the same line, though in opposite directions, and are confounded together. The ray, therefore, which appears single, is, in fact, double, being composed of the incident ray proceeding to the mirror and the reflected returning from it. These rays may, however, be separated by so holding the mirror that the incident ray, *a m*, shall fall *obliquely* upon it, in which case the reflected ray, *m b*, is thrown off in the opposite direction. If a line be drawn from the point of inci-



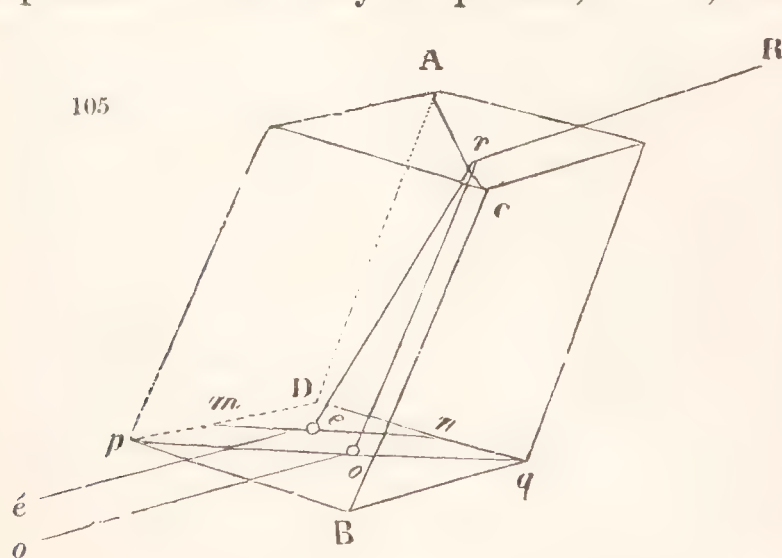
dence, perpendicular to the mirror (as the line $m r$), it divides the angle of incidence from the angle of reflection, and both are seen to be equal.

When rays of light fall upon a concave mirror, they are reflected as if from a series of planes tangents to that surface, and may thus be *converged* to a point or focus; when, on the other hand, the rays fall upon a convex mirror the convergency of the rays is diminished, and their divergency increased.

§ 13. DOUBLE REFRACTION AND POLARIZATION OF LIGHT.

IN all cases of the *ordinary* refraction of light, the ray by which we see an object through a refracting medium, although bent, yet, in pursuing its course to the eye, does not quit a plane perpendicular to the refracting surface: the plane in which the eye, the object, and the point on the surface of the medium in which the object is seen are contained, is a vertical plane. (HERSCHEL'S *Discourse*, p. 30.) But there are certain *crystalline* substances, as rock-crystal, &c., but especially *Iceland spar*, which possess the remarkable property of *doubling* the image seen through them in certain directions; so that, instead of seeing one, we see two, side by side, when such a crystal is opposed between the object and the eye: and if a ray, or small sunbeam, be thrown upon a surface of this substance, it will, on traversing it, be split into two, making an angle with each other, and each pursuing its own separate course.

Having obtained a rhomb of Iceland spar, fit for these experiments, place it, as shown in fig. 105, above a sharp line, and look through it with the eye about R. The line will appear doubled, like $m n p q$. So also a dot will be doubled, as $e o$. If we cause a ray or pencil of light, R, r , to fall upon the surface of the rhomb, it will be separated into two rays or pencils, $r o r e$, each of which will emerge from



the rhomb at o and e , in the directions $o o'$ and $e e'$ parallel to $R r$. The ray $R r$, therefore, has suffered *double refraction* in passing through the rhomb: and as the very same phenomena will take place by making the ray $R r$ fall at the same incidence and in the same direction, relative to the summit A, upon any point of the faces, it is

manifest that the double refraction cannot arise from any difference of density in different parts of the rhomb. (*Library of Useful Knowledge*, Art. LIGHT.)

Of the doubly-refracted rays, *one* appears to follow the same rule as if the substance were glass or water, and retains the plane perpendicular to the refracting surface: the other ray, on the contrary (which is therefore said to have undergone *extraordinary refraction*) does quit that plane, and its deviation becomes subject to a new law. It has, however, been demonstrated by Fresnel, that in double refraction by crystalline bodies, neither of the rays follows the ordinary law, but both

undergo a deviation from their original plane, and acquire new properties; this is the case with respect to Iceland crystal: we may, however, continue the terms *ordinary* and *extraordinary ray*, for convenience sake.

Certain effects accompanying double refraction, led Newton to suppose that a ray of light, after emerging from the crystal, acquires *sides*; that is, distinct relations to surrounding space, which it carries with it through its whole subsequent course, and which give rise to those complicated and curious phenomena now known under the term *polarization of light*. This idea, however, appeared so extraordinary, and, as Herschel remarks, offered so little handle for further inquiry, that the subject dropped, till Malus, in 1810, announced the discovery of the *polarization of light by ordinary reflection*, at the surface of a transparent body. He found that when a beam of light is *reflected* from the surface of such a body, *at a certain angle*, it acquires the same singular property which is impressed upon it in the act of double refraction, and the phenomena of polarization are in this way more conveniently exhibited.

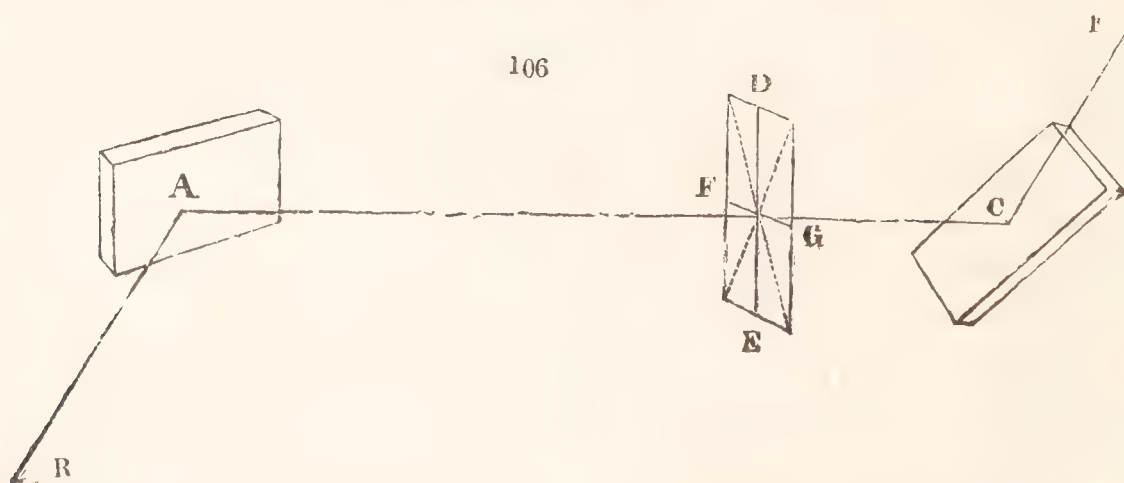
In general, when a ray of light is reflected from a pane of plate-glass or other polished surface, it may be reflected a second time from another surface; it will also pass freely through transparent bodies: but if a ray of light be reflected from a pane of plate-glass, at an angle of 57° , it is rendered incapable of reflection at the surface of another pane of glass, in certain definite positions, but is reflected by it in other positions: it also loses the power of passing through some transparent bodies in certain positions whilst in others it is freely transmitted by them.

If a prismatic crystal of transparent brown *tourmaline*, be cut longitudinally (that is, parallel to the axis of the prism) into plates about the thirtieth of an inch thick, and the surfaces polished, luminous objects may be viewed through them. If one of these plates be held perpendicularly between the eye and a candle, and turned slowly round in its own plane, no change will take place in the image of the candle; but, if the plate be held in a fixed position, with its axis or longitudinal section vertical, when a second plate is interposed between it and the eye, parallel to the first, and turned slowly round in its own plane, a remarkable change is observed in the nature of the light, for the image of the candle vanishes and reappears alternately at every quarter of a revolution of the plate, varying through all degrees of brightness, down to total, or almost total evanescence, and then increasing again as it had before decreased. These appearances depend upon the relative position of the plates: when their longitudinal sections are parallel, the brightness of the image is at its maximum, and when they cross at right angles it vanishes. Thus, the light, in passing through the first plate of tourmaline, has acquired a property totally different from the direct light of the candle: the direct ray would have penetrated the second plate in all directions, whereas the refracted or *polarized* ray penetrates it in certain positions only, and in others is wholly obstructed. The plate of tourmaline therefore becomes, when applied as above directed, a test of the polarization of the ray. If we now look at the two images produced by the Iceland spar, through a plate of tourmaline, it will be found, that as the tourmaline revolves, the images vary in their relative brightness; one increases in intensity till it arrives at a maximum, whilst the other diminishes till it vanishes, and so

on alternately at each quarter of a revolution, showing that *both of the images are polarized* in opposite directions, for in one position the tourmaline transmits the ordinary ray, and reflects the extraordinary; and after revolving 90° , the extraordinary ray is transmitted, and the ordinary ray is reflected. (*Connexion of the Physical Sciences*, by Mrs. SOMERVILLE, § xxi.)

If a pane of plate-glass, with its lower side blackened, or lying upon a piece of black cloth, be placed on a table, and a candle near it, the rays of which fall upon the glass at an angle of 57° , it will be found that they are reflected from the surface in a polarized state, for, on viewing the image through the revolving slice of tourmaline, it will disappear at every quarter of a revolution. It is also found that this polarized ray is incapable of being reflected a second time from another plate of glass, placed at the same angle. If, for instance, the second plate be so placed as to make an angle of about 57° with the reflected ray, the image of the first pane will be reflected in its surface, and alternately illuminated or obscured at every quarter of a revolution of the second plate, according as its plane of reflection is parallel or perpendicular to the plane of polarization. Hence, polarized light is shown to be incapable of reflection in a plane at right angles to the plane of polarization.

These, and some other curious phenomena of polarized light, are easily shown by the following arrangement of apparatus. Let two plates of glass, blacked on the back, A c, be arranged as in the following diagram, fig. 106, so that the rays from a candle at R, falling upon the first or *polarizing* plate, A, at its angle of polarization, may not be reflected by the second or *analyzing* plate, c. This adjustment may be made by looking into c in the direction of Fc, and finding the image of the candle wanting; then



take a thin film of mica, or of sulphate of lime, D E F G, and place it between the two plates perpendicular to the polarized ray. It will then be found, on turning this plate upon its axis, that the image of the candle disappears, and reappears at each quarter of a revolution; or, in other words, that in certain positions the crystalline plate *depolarizes* the ray. Common glass is generally incapable of effecting this depolarization, but it acquires the depolarizing power when submitted to pressure, or heated, or when it has been heated and very suddenly cooled; the influence of its particles upon those of light becoming then analogous to crystallized bodies. If we now view the polarized image through a plate of tourmaline, with the interposed plate of mica, a succession of beautiful colors will appear in certain positions of the mica, depending upon the thickness of the

plate: these colors succeed each other in definite order, and are complementary to each other.

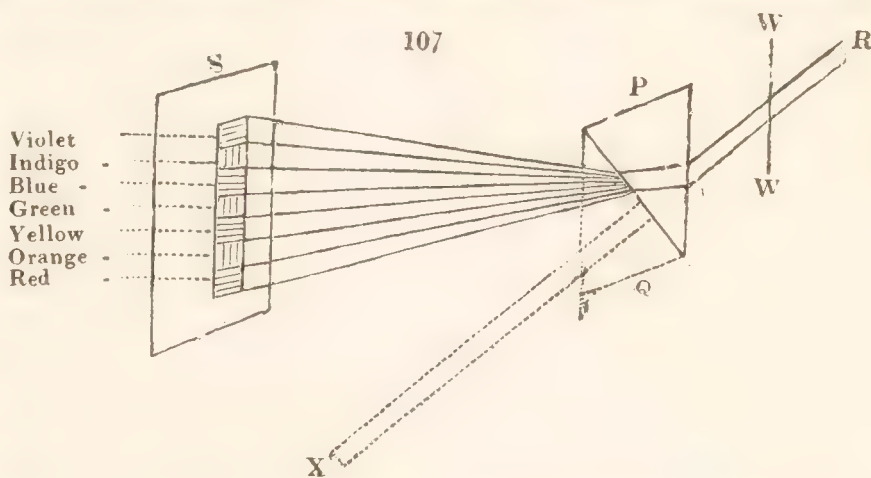
Different reflecting surfaces polarize light at different angles: thus the angle for water is $53^{\circ} 11'$; for glass $56^{\circ} 45'$; for rock crystal $56^{\circ} 58'$; for Iceland spar $58^{\circ} 51'$; for diamond $68^{\circ} 1'$; for sulphur $63^{\circ} 45'$.

In the preceding details, my object has been merely to explain the meaning of the term *polarization*, as applied to certain properties of light; those who would pursue the inquiry will find it amply treated of in the communications of Sir David Brewster to the Royal Society (*Phil. Trans.* 1813, &c.), and in various treatises to which references are given in the authorities which I have had occasion to quote. I must also refer to the same sources, for the discussions to which the investigations connected with the subject have given rise, respecting the nature of light; they are extremely curious and important, especially as illustrative of the applications of the undulatory theory.

§ 14. DECOMPOSITION OF LIGHT.

THAT a sun-beam, in passing through certain dense media, gives rise to a series of brilliant tints, similar to those of the rainbow, was known in the earliest ages, but Newton first explained and investigated the phenomena. He admitted a ray of light, R, fig. 107, through a hole in the window-shutter, w, of a dark room, and caused it to fall upon a glass prism, P, by which it was refracted, and resolved into *seven* colors, which formed an oblong image or *spectrum* upon the white screen, s, in the order represented, namely, red, orange, yellow, green, blue, indigo, and violet.

Had the ray proceeded straight onwards it would have formed a luminous spot at x, it is, therefore, seen that of these colored rays, the *violet* have undergone the greatest refraction, and the *red* the least, and that *they are arranged in the*



order of their refrangibility. Newton submitted each of these rays to repeated refractions, but found that they were not resolvable into simpler colors; but, on causing them to pass through a second prism in an inverted position Q, or by collecting them into one focus by means of a lens, they were reunited and again produced *white light*; whence he inferred white light to consist of these seven simple or primitive colors. With the prism which he used, (of flint glass,) the respective lengths of the colors (dividing the spectrum into 360 parts) were as follows:—red 45, orange 27, yellow 40, green 60, blue 60, indigo 48, violet 80. These spaces, however, cannot be accurately defined, as the colors imperceptibly shade into each other: they also vary with prisms of different substances. The composition of white light by the union of the above colors, may be also shown by mixing seven different powders, having the colors and proportions mentioned; or more readily, by painting the

rim of a wheel with the seven colors, which, when in very rapid motion, appears white, or nearly so*.

The *colors* of bodies were referred by Newton to their relative absorbent and reflective powers, in respect to these rays; he supposed *black* surfaces to absorb, and *white* to reflect them all, and that other colors are produced by the absorption of all the rays except those of the observed color, which are presumed to be reflected. And in respect to transparent media, those which are colorless suffer the light to pass unchanged, while those which are colored, transmit some rays, and absorb others. The absorption of colored rays, therefore, by certain media, furnishes another means of analysing light, and from experiments conducted in this way, Sir David Brewster concludes that the only colors of the spectrum which can be properly called *simple*, are the red, yellow, and blue; that they are concentrated in those parts of the spectrum where each appears, but that they are also spread more or less over the whole, and that the orange results from a mixture of red and yellow; the green, from a mixture of yellow and blue; and the violet and indigo from red and blue, with a trace of yellow.

The length of the spectrum depends upon the nature of the prism or refracting medium; thus, if obtained by a hollow prism of glass, filled with oil of cassia, it is much longer than when glass only is used; hence the oil of cassia is said to *disperse* the rays more than glass, or to have a greater *dispersive power*. In such cases, also, the colored spaces bear a very different ratio to each other.

It appears from the experiments of Sir W. Herschel, (*Phil. Trans.*, 1800,) that the greatest *illuminating* power of the spectrum is in the brightest yellow, and that it decreases towards either extremity, the blue and red being nearly equal, and the violet inferior to both.

A curious fact respecting the prismatic spectrum, when very perfect, and the sunbeam small, was discovered by Professor Fraunhofer, of Munich; he observed it to be irregularly subdivided by a number of dark bands or lines; they are so narrow as to escape observation without great care; they are seen when the spectrum is received upon the object-glass of a telescope, or by viewing a narrow slit between two nearly-closed shutters, through a very perfect prism, held close to the eye, with its refracting angle parallel to the line of light, and give it the appearance of a striped riband. They are always found in the same parts of the spectrum, of the same breadths and intensities, and preserving the same relations to one another. They are very numerous, amounting to some hundreds; from these, Fraunhofer selected seven, and determined their distances so accurately, that they form invariable points of reference for measuring the refractive powers of different media. They are also seen in the light of the stars, in electric light, and in the flame of combustible substances, though in each case differently arranged, each having a system of them peculiar to itself, and remaining the same under all circumstances.

* The impression of light upon the retina of the eye continues for about an eighth part of a second, so that a luminous point revolving with a velocity sufficient to complete the circle within that time, appears not as a point, but as a circle of light, the impression made on it in every point of its revolution being retained for the above time. Many familiar appearances are referable to this principle.

§ 15. CHEMICAL EFFECTS OF THE SOLAR RAYS.

THE object of the preceding sections has been to give a mere outline of the principal physical properties of light. We may now proceed to the consideration of some other phenomena connected with, or dependent upon, the solar rays.

No one can have failed to observe the differences between *vegetables* thriving in the full enjoyment of solar light, and those which grow in obscure situations, or which are entirely deprived of its agency. The former are of brilliant tints, the latter dingy and white; in the one, the various secretions come to perfection; in the other they are either modified or disappear. Of this, numerous familiar instances might be cited, especially among our esculent vegetables. The shoots of a potato produced in a dark cellar are white, straggling, and differently formed from those which the plant exhibits under its usual circumstances of growth. Celery is cultivated for the table by excluding the influence of light upon its stem, which is effected by heaping the soil upon it so as to screen it from the solar rays; but if suffered to grow in the ordinary way, it soon alters its aspect, throws out abundant shoots and leaves, and instead of remaining white and of little taste, acquires a deep green color, and a bitter flavor. The interior, or heart of endive is not eatable, unless protected from light; if exposed to it, it becomes disagreeably bitter and tough. The heart of the common cabbage is another illustration. The rosy and colored aspects of the side of fruits exposed to the sun are referable to the same cause. Changes yet more remarkable have been observed in plants vegetating entirely out of the access of light. In visiting a coal mine, Professor Robinson found a plant with a large white foliage, the form and appearance of which were quite new to him: it was left at the mouth of the pit, when the subterranean leaves died away, and common tansy sprang up from the root.

In the *animal creation* the influence of light is equally evident. It is curious to remark the dull and dingy tints of polar and subterranean animals, as contrasted with the gaudy and brighter colors of those which inhabit the tropical regions of the globe, and enjoy the full sunshine. In the human species, too, a due quantity of light is requisite to health; miners are generally pallid and unhealthy; and the inhabitants of the alleys and courts of London indicate a similar want of its beneficial influence; though in these cases, bad air and poor diet also contribute to the morbid pallor.

In reference to the above and similar effects of light upon plants, there can be little doubt that they chiefly depend upon its power of modifying the chemical changes which are constantly carrying on in the vegetable kingdom; but the common operations of the laboratory also furnish some striking illustrations of *the influence of light in modifying and promoting the chemical agencies of bodies*.

Hydrogen and *chlorine* are two gases, which, when mixed and kept in the dark, are nearly without action; but if exposed to the light of day, they soon act upon each other, and unite to form *hydrochloric acid*; and if the sun shines directly upon the bottle containing them, it not unfrequently happens that they inflame and explode in consequence of the exaltation of their mutual affinities by the agency of the solar rays. We have an

analogous instance in *chlorine* and *carbonic oxide gas*, which, when mixed together, remain without action till exposed to light; they then combine chemically with diminution of volume, and produce a compound, which, from the mode of forming it, has been termed *phosgen* gas. In the same way also, chlorine and water gradually react upon each other in the sunshine, forming hydrochloric acid and evolving oxygen, but are mutually inactive when kept in the dark.

Some of the salts of gold and of silver, especially their chlorides, are remarkably susceptible tests of the chemical agency of light: the *nitrate of silver* may be selected by way of illustration. If a piece of paper be dipped into a solution of this salt, and kept in the dark, it suffers no apparent change; but if exposed to light, it soon becomes purple, brown, and black, changes of color depending upon a chemical change suffered by the salt. A pretty experiment, showing the action of light upon nitrate of silver, was devised as far back as the year 1800 by Mr. T. Wedgwood (*1st Royal Inst. Journ.*, i. 170): a piece of paper, or other convenient material, was stretched upon a frame and sponged over with a solution of the salt; it was then placed behind a painting upon glass; and the light, traversing the painting, produced a kind of copy of it upon the prepared paper; those parts in which the rays were least intercepted being of the darkest hues. This experiment may be regarded as the origin of the art of *Photography*, which, in the hands of Mr. Fox Talbot, Sir J. Herschel, and Mr. Alfred Taylor, has attained a high degree of interest and perfection.

The silver compounds most susceptible of this action of light are those in which certain organic substances are present, and especially tannic or gallic acids, and these sometimes bring out the effect in a very extraordinary way. A sensitive paper, for instance, for receiving images in the *camera obscura* is prepared as follows: it is first washed over with a solution formed by dissolving 60 grains of crystallized nitrate of silver in an ounce of water, and allowed to dry spontaneously: when dry it is to be dipped three or four times in a solution of 10 grains of iodide of potassium (or 5 of the iodide, and 5 of chloride of sodium,) in an ounce of water, and dried by pressure between folds of blotting paper: in this state the image is thrown upon it, (for about a minute or more, according to the intensity of the light,) and no *apparent* effect is produced; but if it now be pinned on a board, and washed over with a solution of 4 grains of gallic acid in an ounce of water, (or even with infusion of galls,) in a few moments the hidden impression comes out. (CHANNING.) Some further details illustrative of this process are given in the annexed note*, extracted from a

* "*Preparation of the Paper.*—Take a sheet of the best writing paper, having a smooth surface, and a close and even texture. The watermark, if any, should be cut off, lest it should injure the appearance of the picture. Dissolve 100 grains of crystallized nitrate of silver in six ounces of distilled water. Wash the paper with this solution, with a soft brush, on one side, and put a mark on that side whereby to know it again. Dry the paper cautiously at a distant fire, or else let it dry spontaneously in a dark room. When dry, or

nearly so, dip it into a solution of iodide of potassium containing 500 grains of that salt dissolved in one pint of water, and let it stay two or three minutes in this solution. Then dip it into a vessel of water, dry it lightly with blotting-paper, and finish drying it at a fire, which will not injure it even if held pretty near: or else it may be left to dry spontaneously.

"All this is best done in the evening by candlelight. The paper so far prepared the author calls *iodized paper*, because it has a uniform pale yellow coating of iodide

communication of Mr. Talbot to the Royal Society in 1841, (*Proceedings of the Royal Society*), and it will again be adverted to under the article SILVER, where also will be found a notice of the *Daguerrotype*, a subject involving some very remarkable effects of light.

As further illustrations of the extraordinary chemical influence of light we may refer to Sir John Herschel's "Researches on the Action of the Rays of the Solar Spectrum on Vegetable Colors," (*Phil. Trans.*, 1840,) and to his discovery of a process, by which paper washed over with a solution of ammoniocrate of iron, dried, and then washed over with a solution of ferridcyanide of potassium, is rendered capable of receiving with great rapidity a photographic image, which, from being originally

of silver. It is scarcely sensitive to light, but, nevertheless, it ought to be kept in a portfolio or a drawer, until wanted for use. It may be kept for any length of time without spoiling, or undergoing any change, if protected from the light. This is the first part of the preparation of *Calotype* paper, and may be performed at any time. The remaining part is best deferred until shortly before the paper is wanted for use. When that time is arrived, take a sheet of the *iodized paper* and wash it with a liquid prepared in the following manner:—

"Dissolve 100 grains of crystallized nitrate of silver in two ounces of distilled water; add to this solution one-sixth of its volume of strong acetic acid. Let this mixture be called A."

"Make a saturated solution of crystallized gallic acid in cold distilled water. The quantity dissolved is very small. Call this solution B.

"When a sheet of paper is wanted for use, mix together the liquids A and B in equal volumes, but only mix a small quantity of them at a time, because the mixture does not keep long without spoiling. The author calls this mixture the *gallo-nitrate of silver*.

"Then take a sheet of *iodized paper* and wash it over with this *gallo-nitrate of silver*, with a soft brush, taking care to wash it on the side which has been previously marked. This operation should be performed by candlelight. Let the paper rest half a minute, and then dip it into water. Then dry it lightly with blotting-paper, and finally dry it cautiously at a fire, holding it at a considerable distance therefrom. When dry, the paper is fit for use. The author has named the paper thus prepared *Calotype paper*, on account of its great utility in obtaining the pictures of objects with the camera obscura. If this paper be kept in a press it will often retain its qualities in perfection for three months or more, being ready for use at any moment; but this is not uniformly the case, and the author therefore recommends that it should be used in a few hours after

it has been prepared. If it is used immediately, the last drying may be dispensed with, and the paper may be used moist. Instead of employing a solution of crystallized gallic acid for the liquid B, the *tincture of galls* diluted with water may be used, but he does not think the results are altogether so satisfactory.

"*Use of the Paper.*—The *Calotype paper* is sensitive to light in an extraordinary degree, which transcends a hundred times or more that of any kind of photographic paper hitherto described. This may be made manifest by the following experiment:—Take a piece of this paper, and having covered half of it, expose the other half to daylight for the space of *one second* in dark cloudy weather in winter. This brief moment suffices to produce a strong impression upon the paper. But the impression is latent and invisible, and its existence would not be suspected by any one who was not forewarned of it by previous experiments.

"The method of causing the impression to become visible is extremely simple. It consists in washing the paper once more with the *gallo-nitrate of silver*, prepared in the way before described, and then warming it gently before the fire. In a few seconds the part of the paper upon which the light has acted begins to darken, and finally grows entirely black, while the other part of the paper retains its whiteness. Even a weaker impression than this may be *brought out* by repeating the wash of gallo-nitrate of silver, and again warming the paper. On the other hand, a stronger impression does not require the warming of the paper, for a wash of the gallo-nitrate suffices to make it visible, without heat, in the course of a minute or two.

"A very remarkable proof of the sensitiveness of the calotype paper is afforded by the fact stated by the author, that it will take an impression from simple moonlight, not concentrated by a lens. If a leaf is laid upon a sheet of the paper, an image of it may be obtained in this way in from a quarter to half an hour.

faint and sometimes scarcely perceptible, is immediately called forth on being washed over with a neutral solution of gold. The picture does not at once acquire its full intensity, but darkens with great rapidity up to a certain point, when the resulting photograph attains a sharpness and perfection of detail which nothing can surpass. To this process he applies the name of *Chrysotype*. (*Phil. Trans.*, 1842, p. 206.)

Scheele was the first to whom the idea occurred of ascertaining whether all the rays possessed similar chemical powers, or whether they belonged more exclusively to one color than to another; and he found, upon refracting a beam by the prism into its primary colors, and throwing them upon a piece of paper prepared with nitrate of silver, that the greatest

“This paper being possessed of so high a degree of sensitiveness, is therefore well suited to receive images in the camera obscura. If the aperture of the object lens is one inch, and the focal length fifteen inches, the author finds that *one minute* is amply sufficient in summer to impress a strong image upon the paper of any building upon which the sun is shining. When the aperture amounts to one-third of the focal length, and the object is very white, as a plaster bust, &c., it appears to him that *one second* is sufficient to obtain a pretty good image of it.

“The images thus received upon the Calotype paper are for the most part invisible impressions. They may be made visible by the process already related, namely, by washing them with the gallo-nitrate of silver, and then warming the paper. When the paper is quite blank, as is generally the case, it is a highly curious and beautiful phenomenon to see the spontaneous commencement of the picture, first tracing out the stronger outlines, and then gradually filling up all the numerous and complicated details. The artist should watch the picture as it develops itself, and when in his judgment it has attained the greatest degree of strength and clearness, he should stop further progress by washing it with the fixing liquid.

“*The fixing process.*—To fix the picture, it should be first washed with water, then lightly dried with blotting paper, and then washed with a solution of *bromide of potassium*, containing 100 grains of that salt dissolved in eight or ten ounces of water. After a minute or two it should be again dipped in water and then finally dried. The picture is in this manner very strongly fixed, and with this great advantage, that it remains transparent, and that, therefore, there is no difficulty in obtaining a copy from it. The Calotype picture is a *negative* one, in which the lights of nature are represented by shades; but the copies are *positive*, having the lights conformable to nature. They also represent the objects in their natural position with respect to right

and left. The copies may be made upon Calotype paper in a very short time, the invisible impressions being *brought out* in the way already described. But the author prefers to make the copies upon photographic paper prepared in the way which he originally described in a memoir read to the Royal Society in February, 1839, and which is made by washing the best writing-paper, *first* with a weak solution of common salt, and *next* with a solution of nitrate of silver. Although it takes a much longer time to obtain a copy from this paper, yet when obtained, the tints appear more harmonious and pleasing to the eye; it requires in general from 3 minutes to 30 minutes of sunshine, according to circumstances, to obtain a good copy on this sort of photographic paper. The copy should be washed and dried, and the fixing process (which may be deferred to a subsequent day) is the same as that already mentioned. The copies are made by placing the picture upon the photographic paper, with a board below and a sheet of glass above, and pressing the papers into close contact by means of screws or otherwise.

“After a Calotype picture has furnished several copies, it sometimes grows faint, and no more good copies can then be made from it. But these pictures possess the beautiful and extraordinary property of being susceptible of revival. In order to revive them and restore their original appearance, it is only necessary to wash them again by candlelight with gallo-nitrate of silver, and warm them; this causes all the shades of the picture to darken greatly, while the white parts remain unaffected. The shaded parts of the paper thus acquire an opacity which gives a renewed spirit and life to the copies, of which a second series may now be taken, extending often to a very considerable number. In reviving the picture it sometimes happens that various details make their appearance which had not before been seen, having been latent all the time, yet nevertheless not destroyed by their long exposure to sunshine.”

blackening effect was produced by the *violet* ray, and that the decomposing or chemical powers of the prismatic *spectrum*, gradually decreased towards the red ray, where scarcely any effect was produced. This result was quite contrary to expectation; for one would, of course, have anticipated the greatest effect in the most luminous part of the spectrum.

It was afterwards discovered by Wollaston and Ritter, (*Phil. Trans.*, 1802, and *Philos. Journal*, iv. and viii.,) that certain *invisible* rays, occupying a place in the spectrum just beyond the violet extremity, possessed a greater power of effecting chemical changes, than the violet rays themselves; and it has, consequently, been inferred that such distinct rays emanate from the sun, possessed, as their place in the spectrum shows, of great refrangibility: and that the colored rays (and their mixture, constituting white light,) derive their chemical powers from the admixture of these highly refrangible and chemically acting rays, which are most abundant at the blue end of the spectrum, and gradually decrease towards the red or least refrangible rays. Thus, it was found that the greatest blackening effect upon the salts of silver was produced just beyond, and out of the violet ray: and that other peculiar chemical effects were also most manifest in the same spot. It must, however, be observed, that the place occupied by these rays in the spectrum depends, in some measure, upon the nature of the medium by which the light is refracted*.

Berard found, that in the focus obtained by concentrating the rays of one-half of the spectrum (the red end), chloride of silver was not blackened, though the light was very brilliant; but that, in the darker focus from the violet half, it was immediately discolored. (GILBERT'S *Annalen der Physik*, xlvi. 376.) Seebeck, by exposing chloride of silver to the red ray, found that it gradually acquired a pale rose color; and that the rays colored by transmission through colored glasses, produced the same general effects as the differently colored rays of the spectrum. He also found that a piece of paper, dipped in a neutral, and not too-concentrated solution of gold (which is reduced by light), underwent no change when preserved in the dark, provided it had not been previously exposed to light; but that, if exposed for a short time to the sun's rays, though not at the moment discolored, and then kept in a dark place, it gradually became purple, and the gold was reduced. He further ascertained the protective influence of the red and orange rays upon the chemical influences of light; thus, paper imbued with salts of silver underwent no change when long exposed to the solar rays in tubes of orange-colored glass; and chlorine and hydrogen did not combine in red glass tubes, nor under the influence of light transmitted through solution of bichromate of potassa. (DRAPER. *Phil. Mag.*, xvi. 81.) In the manipulations of photography lamps glazed with yellow, orange, or red glass, do not affect the unprotected paper. (SEEBECK'S *Essay is published in* GOETHE'S *Farbenlehre. Quart. Review*, x. 427.) Herschel observed that lime water added to solution of chloride of platinum only afforded a precipitate in white or violet, and not in yellow or red light. Etherial solution of perchloride of iron is changed into pro-

* Sir J. Herschel has rendered it probable that the solar spectrum includes rays still more refrangible than the violet: they retain a peculiar *lavender* or grey color even when concentrated.—*Phil. Trans.*, 1840, p. 19.

tochloride behind white and blue, but not red glass; and etherial solution of corrosive sublimate affords calomel under the influence of the former, but not of the red light. (A. VOGEL.) Solution of peroxalate of iron is decomposed by white, violet, and blue light into carbonic acid and prot-oxalate; but neither by red light, nor by a boiling heat. (DÖBEREINER.) Grotthuss (*Phys. Chem. Schrifte.*) states that the blue solution of iodide of starch is bleached under the influence of white, green, and yellow light, yielding hydriodic acid; that red and blue light affect it but little, and that it is unchanged in violet light. These instances may here suffice as to the general chemical influences of the various modifications of light; a number of other cases will be adduced under the history of the individual substances and processes, which are particularly affected by it.

Ritter (GILBERT'S *Annalen*, vii. and xii.) and Davy (*Elem. Chem. Phil.*) have assumed that the opposite ends of the spectrum possess opposed chemical powers, something like the opposed electrical poles, but of this we have, as yet at least, no satisfactory experimental evidence: it is true that Wollaston found a piece of paper stained yellow with tincture of guaiacum, to become green in the violet ray, and again yellow in the red; but he afterwards observed that the mere heat of the red ray produced the effect; and many vegetable colors are as effectually bleached by heat as by light.

The general effects of the solar rays in producing chemical and electrical changes have been also elaborately studied by E. Becquerel. (*Ann. Ch. et Ph.*, Nov., 1843.)

Many years ago, Morichini thought that he had communicated *magnetism* to steel wires, by exposing them to the rays of violet light. So curious a result attracted much notice, and his experiments were repeated by several eminent philosophers with very various success: it was generally, however, presumed that he was mistaken in his conclusions, and that the needles had acquired magnetism from some other source. The subject was afterwards resumed by Mrs. Somerville, (*Phil. Trans.*, 1826,) who, from a series of apparently well-conducted experiments, arrived at the same conclusion as Morichini. It must however, be confessed, that there are many difficulties in the way of attaining perfectly unexceptionable results in these experiments; and whether magnetism is, or is not, producible by the sole influence of light, is a question not definitively settled, unless, indeed, the experiments of Messrs. Riess and Moser (*Edin. Journal of Science*, II., 225,) be considered conclusive in disproving it*.

§ 16. OF RADIANT MATTER AS A SOURCE OF HEAT.

Different parts of the prismatic spectrum have different heating powers.—If we cause the spectrum to fall upon a sheet of paper, and gradually pass the hand through it, from the violet to the red end, we shall perceive the latter to be sensibly warmer than the former; and, on applying a delicate thermometer in the differently colored rays, it will be found scarcely affected by the blue; in the green it rises; and in the red, shows an increase of several degrees of temperature. Assuming the

* The decomposition of light by thin plates, and the phenomena of *diffraction*, are necessarily here passed over: the student wishing to pursue these subjects is therefore referred to treatises expressly relating to them.

heating power of the violet rays = 16° , that of the green is = 26° , and of the red = 55° .*

The observation of this fact suggested to Sir W. Herschel the probability of the heating power of the spectrum extending *beyond* the red ray, and, on applying a thermometer just out of the red ray, and beyond the limits of the visible spectrum, this was found to be the case. A thermometer *in* the red ray rose *seven* degrees in ten minutes, but just *beyond* the red ray, the rise in the same time was *nine* degrees. (*Phil. Trans.*, 1800. See also the repetition of these experiments by Sir H. Englefield, and by M. Berard. THOMSON'S *Annals*, II., 136.)

In these, as in the former experiments, the effects are modified by the nature of the prism used to refract the light: when it is of flint glass the phenomena are as above described; but, with crown glass, water, and other refracting media, the position of the heating or calorific rays varies.

It appears, then, that the radiant matter of the sun is resolvable, by refraction, into three distinct sets of rays; those producing *color*; those which effect certain *chemical changes*; and those which excite *heat*; the chemically acting rays are the *most* refrangible, the calorific rays the *least* so, and the colorific rays, or those producing light and color, possess a *mean* degree of refrangibility. All these rays are susceptible of refraction and reflection, as is proved by their concentration into a focus by a concave mirror or a lens; in which case, in consequence of their different refrangibilities, the heating and chemically acting focus is probably not absolutely identical with the luminous focus. From the experiments of Berard, Melloni, and Forbes, the chemically acting and the heating rays are also susceptible of polarization.

§ 17. TERRESTRIAL RADIATION, AND THE INFLUENCE OF VARIOUS SURFACES UPON THE RECEPTION AND EMISSION OF RADIANT MATTER.

WE use the term *terrestrial radiation*, to designate the heat and light thrown off by terrestrial bodies under certain circumstances, especially at high temperatures, as when they are red-hot, or burning; that is, in a state of *ignition, incandescence, or combustion*. We also well know that terrestrial heat radiates from bodies at temperatures far below those required for ignition, as, for instance, from a vessel filled with hot water. These subjects may be discussed under the head of *terrestrial radiation*.

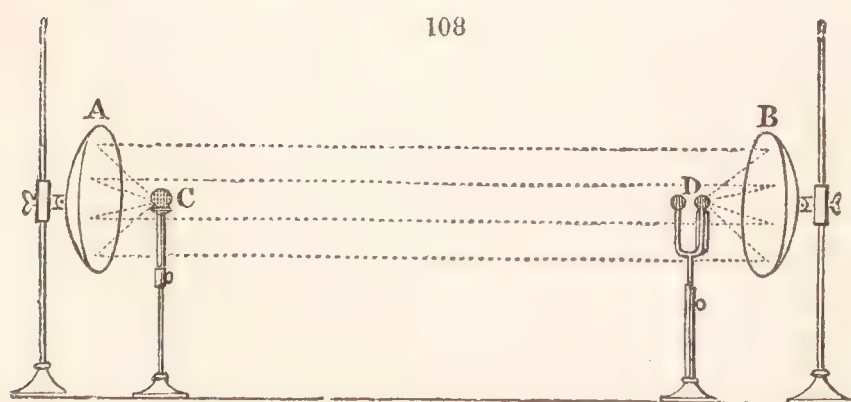
The rays which emanate from heated bodies, whether attended or unattended by light, may be *reflected* in the same way as the solar rays, and the phenomena connected with this kind of radiation are, in many respects, extremely curious and important: they are also susceptible of many economical applications, for in this country it is to radiant heat that we are chiefly indebted for the warmth and comforts of our apartments in winter; the construction of our grates, and fire-places in general, being such as to carry away the whole current of the heated air by the chimney, and prodigally waste it in the atmosphere; they consequently produce their warming effects, by the heat which emanates from the burning fuel and heated surfaces, and is projected or radiated upon the surrounding bodies in the room.

* Hence the idea of the different-colored rays consisting of light in combination with different proportions of heat.

Several important facts upon the subject of the radiation of heat were established many years ago by Scheele (in his treatise on *Air and Fire*, originally published in 1777). He observed, that radiant heat passes through air without communicating heat to that medium, and that it is not intercepted by currents in the atmosphere. He then proceeded to ascertain how far it coincided with *solar* heat, in passing through glass, and found that, although the *light* of a fire or of a candle passed through it, their *heat* was arrested, or stopped in its progress. It was thus thought that a decided difference was established between solar and terrestrial heat; but we shall find that, in reference to this experiment, it is rather apparent than real, and partly due to the small quantity, or intensity of the latter, as compared with the former. He also found that, when a *glass* mirror is held before the fire, the light only is reflected, while the heat is absorbed, and the mirror itself becomes hot; but when for glass we substitute a mirror of *polished metal*, then both the heat and the light are reflected, and the metal itself not heated: if, however, the surface of the metal be covered with some other substance, if it be smoked, for instance, by holding it over a burning candle, then the surface *absorbs* the rays of heat, and the mirror of metal, like that of glass, becomes itself hot.

These observations of Scheele led Leslie and others into the same path of inquiry, and we have, upon the whole, a very satisfactory series of experiments upon the subject, of which the following is an outline, as far as the principal facts are concerned:—

That this heat radiates from bodies in right lines, and is susceptible of reflection, is shown by placing two polished concave mirrors, made of planished tin, or, what is better, of plated copper, exactly opposite to each other, and about ten feet asunder. For experiments upon a large scale, the mirrors should be at least of two feet diameter, plated with silver and burnished; but planished tin-plate mirrors or reflectors of one foot are sufficient for all common illustrations. A heated body, such, for instance, as an iron ball, or a flask of boiling water, is placed in the focus of one mirror, and an air-thermometer in that of the other*. The rays of heat then impinge on the one mirror, and are *reflected*, consistently with the property of parabolic mirrors, in parallel lines, so as to fall upon the opposed mirror, whence they converge to its focus, in which is the thermometer, and which is affected proportionately to the heat of the original radiating body.



Let A, fig. 108, represent the first mirror; B the second; C the heated sphere or flask, and D the air-thermometer; the dotted lines show the direction of the calorific rays.

To prove that the

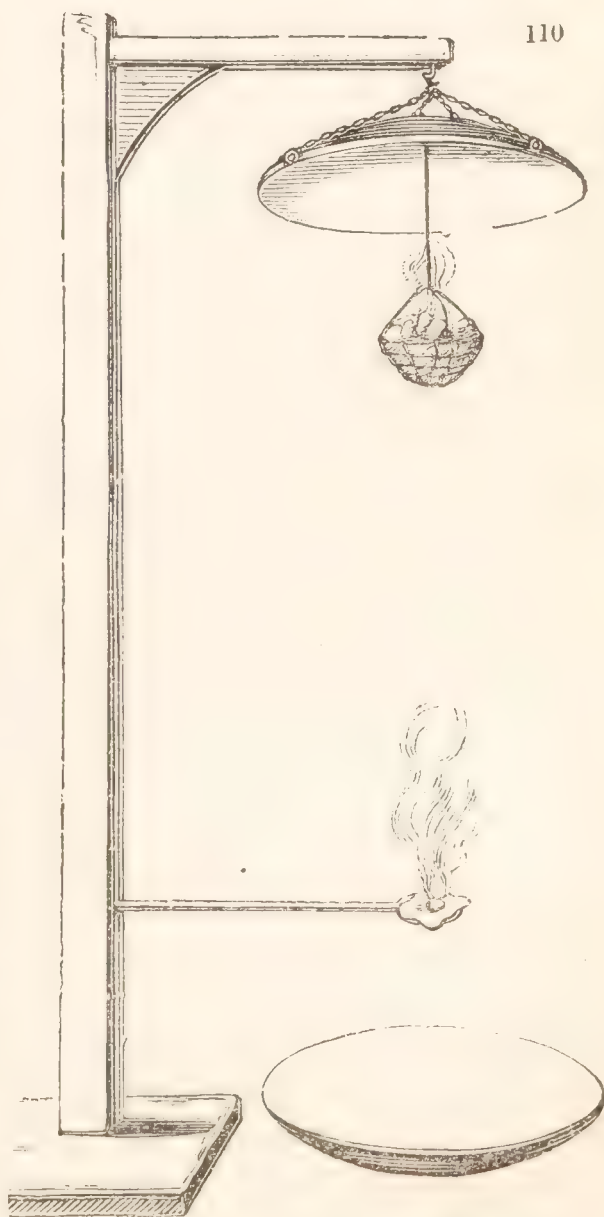
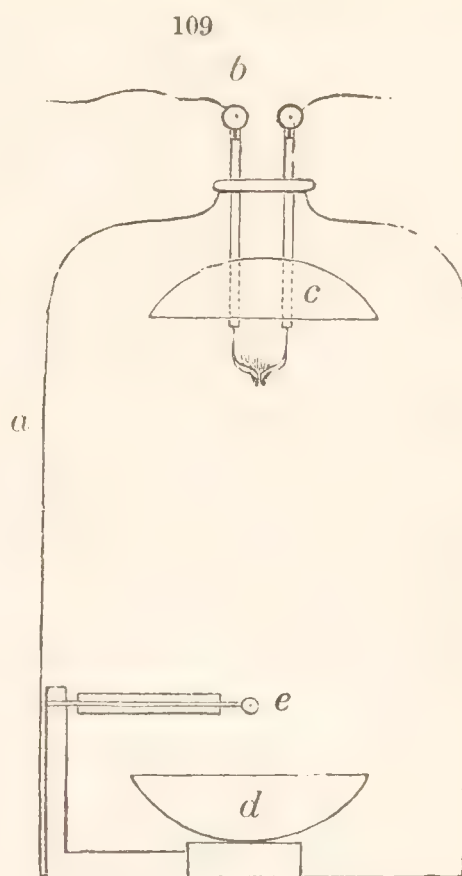
* The foci of the mirrors are best found by the help of a lighted candle, the heating focus closely corresponding with the luminous one; and in these experiments the *differential thermometer* above described is

most satisfactorily employed, for it is not affected by currents or general changes in the temperature of the room in which the experiments are made.

thermometer is not affected by the *mere proximity* of the heated body, independently of any actual *reflection*, let a sheet of pasteboard be held between the mirror *B* and the thermometer; the latter will immediately indicate the absence of the quantity of heat it before received, notwithstanding the source is as near to the bulb as it was before. If we even carry the ball a little out of the focus of the mirror *A*, by advancing it gently towards the thermometer, a diminution of heat will be perceived in the latter, in consequence of the disturbance of the most favorable arrangement for reflection. Indeed, the distance between the heated ball and the air-thermometer is such, that notwithstanding the delicacy of the latter instrument, it would not be affected, as may again be shown by removing one or both of the mirrors, and leaving the ball and thermometer in their same relative positions.

Radiation goes on from surfaces in all elastic media, and in vacuo, and is no way connected with aërial waves or pulsations. By igniting points of charcoal by the voltaic battery in the focus of a small mirror confined in the exhausted receiver of the air-pump, Sir H. Davy found, that the receiver being exhausted to $\frac{1}{120}$, the effect upon the thermometer in the opposite focus was nearly three times as great as when the air was in its natural state of condensation. *a*, fig. 109, is the receiver, *bb* the insulated wires connected with the voltaic apparatus igniting the charcoal in the focus of the upper mirror *c*. In the focus of the lower mirror *d* is the thermometer *e*. But a great part at least of this increased effect is probably due to the increase of heat sustained by the charcoal, when thus ignited in vacuo, as compared with that which it acquires in the air.

If, for the hot bullet, or flame of a candle, or flask of boiling water, we substitute some more copious source of heat, the effects will be pro-



portionately great. If we, for instance, place a wire-basket full of burning charcoal, or a piece of red hot iron in one focus, and a piece of phosphorus in the other, the latter will be immediately inflamed; in the same way fulminating silver may be exploded, a mixture of chlorate of potassa and sulphuret of antimony inflamed, and even gunpowder kindled. And for such experiments we may adopt Sir H. Davy's plan of placing the mirrors vertically, as shown in fig. 109; the little chafing-dish is in the focus of the upper mirror, so that all the heat that reaches the lower mirror, and is concentrated in its focus, must be radiant and reflected, for the current of heated air will pass upwards and be lost.

For the conjugate mirrors we may occasionally substitute a sheet of burnished gold or silver paper, twisted up into the form of a truncated cone, with the metallic surface inwards: on holding its larger end towards a clear fire, or before a heated ball of iron, the radiant heat will be reflected so as to form a focus beyond the smaller end, where a piece of phosphorus or a lucifer match may be kindled.

The intensity of the calorific, as well as that of the luminous rays, decreases as the squares of the distance from the substance whence they emanate. A thermometer, for instance, placed at the distance of one foot from a heated body, will indicate the reception of four times more heat than at two feet, of nine more than at four feet, and of sixteen times more than at three feet. (See fig. 99.)

If we substitute a *cold body* for the heated one, a lump of ice, for instance, sprinkled over with salt, or a thin glass flask containing a mixture of snow and salt, we shall then observe the thermometer in the opposite focus to be affected by *cold*; and this experiment has sometimes been adduced to prove that cold is a distinct form of matter. It has been supposed that highly attenuated emanations are at all times passing off from the surfaces of all bodies, under the form, and producing the effects of, *radiant matter*, the temperature excited by which depends upon that of the emanating body: that hot bodies radiate heat: that we perceive no effect from bodies at common temperatures, because their radiant matter is of the same temperature as that of the thermometer or substance upon which they fall: but that cold bodies, on the contrary, throw off cold radiant matter, and hence their effect upon the thermometer. It has been assumed that the actual radiation of cold is proved by placing a plate of snow or bruised ice near the face, when an effect of cold is immediately perceived, and may be intercepted by a sheet of paper or other screen: that *temperature* therefore is merely a relative term: and that we may suppose ourselves in a temperature so high, that red-hot iron would radiate cold; or, again, in a temperature so low, that ice would radiate heat.

Sir H. Davy observes, in reference to this subject, which he calls the *apparent* radiation of cold, "that if it be supposed that rays capable of producing heat emanate from all terrestrial bodies, but in quantities greater in some increasing proportion as their temperatures are higher, then the introduction of a cold body into the focus of one mirror, ought to diminish the temperature of a thermometer in the focus of the other, in the same manner as a black body placed in one focus would diminish the quantity of light in the other focus; and the eye is to the rays producing light, a measure similar to that which the thermometer is to rays

producing heat." (*Elements*, p. 206.) Dr. Turner observes, that "the thermometer has its temperature lowered because it emits more rays than it receives, and it rises when the ice is removed, because it then receives a number of calorific rays, radiated by the warmer surrounding objects which were interrupted by the ice whilst it was in the focus." Daniell says, "the thermometer is the hotter body, and radiating its heat upon the nearest mirror, the rays are projected upon the second, and collected in the focus, where they are absorbed by the ice; and as no adequate return is made, the temperature of the thermometer necessarily falls."

INFLUENCE OF DIFFERENT SUBSTANCES AND SURFACES UPON THE RECEPTION, TRANSMISSION, AND EMISSION OF RADIANT HEAT. It has been stated, that if a *polished metallic* mirror, of a concave or parabolic form, be held opposite the fire, it will give a heating focus, but that the mirror itself is long before it becomes sensibly warm; that is, the heat which impinges upon it, is immediately thrown off or *reflected*. If we now cover the surface of the mirror with an *unmetallic* coating, or if we merely roughen the surface, and then hold it towards the fire, a very different effect ensues, and now, the greater part of the radiant heat, instead of being thrown off, is *absorbed*, and soon heats the mirror, as for instance, with a mixture of chalk or lampblack and diluted glue or gumwater.

Here, then, the *receptive* powers of surfaces, in regard to radiant matter, are shown materially to depend upon their nature or mechanical texture. In further illustration of this subject, a simple experiment may be made with the differential air-thermometer: let one of the glass bulbs, for instance, be nicely covered with a bright coating of gold-leaf, and leave the other in its usual state: place the instrument thus prepared upon a table, and bring a hot poker near it, taking care, however, that it is equally distant from both bulbs, or, if anything, rather nearer the metallic than the glass surface. Under these circumstances it will be found, that by far the greatest effect of heat is produced upon the *glass* ball, from which the fluid in the tube immediately recedes, notwithstanding heat is equally applied to the gilt ball; the latter, however, refuses to absorb it, while the former imbibes it, and has its temperature proportionately augmented. If, instead of leaving the ball clean, it be covered with a thin coat of whitewash, or of lampblack, its receptive power will be still greater.

Although the *texture* of the surface is shown to be materially concerned in these results, it does not appear that *color* interferes; black-wash and white-wash are equally receptive of *terrestrial* radiant heat; nor does it appear to be absorbed in larger proportion by any one color than by another. (BACHE, *Journ. Franklin Institute*; May and November, 1835.) Dr. Stark indeed (*Phil. Trans.*, 1836) has endeavoured to show that *color* does interfere in these cases; and he gives some curious statements respecting its influence upon the reception of *odors*; but it is possible that the texture and composition of the materials employed may affect the results; just as *white* silk is a much better insulator of electricity than *black* silk; not on account of color, but of dye-stuff.

With regard to *solar* radiant heat, however, the case is different, and, as common experience teaches, *black* surfaces absorb it much more greedily

than white, and *the temperature produced appears to be proportionate to the intensity of color**. If pieces of cloth of different colors be exposed to the sunshine upon the surface of snow, the dark colors will sink into it, in consequence of the heat which they produce; the lighter colors scarcely effect the thawing of any portion; and white remains inactive. The difference between a white and black hat in heating the head, and between dark and light-colored clothing in general, is well known to those who are much exposed to the summer's sun. Paint the bulb of one thermometer black, and of another white, and expose them to the sunshine; the former will indicate a higher temperature than the latter. A similar but more striking experiment may be made with the differential thermometer. Blacken one of the bulbs, and leave the other clean and transparent; if the instrument thus prepared be exposed to the sunshine, the excess of heat in the blackened ball is immediately indicated by the recession of the liquid from it to the clean ball. If the air thermometer be small and delicate, it is even susceptible of the mere impression of daylight, which, slightly augmenting the temperature of the black ball, depresses the fluid in the tube annexed to it. Hence the differential thermometer, thus constructed and applied, has been called a *photometer*†. Another illustration of this effect of solar rays, consists in placing a glass tube containing alcohol or ether in their focus, when collected by a lens; they traverse the transparent medium without heating it; but upon putting a piece of black paper into the liquid, or a piece of charcoal, or a strip of black wood, it immediately boils. In this way water may be heated by directing the focus of a lens or mirror, exposed to the sun, upon good receptive and opaque surfaces immersed in it.

In many of the above statements there seems to be a manifest *difference* between solar and terrestrial radiant heat; but this is probably rather apparent than real; in the solar beam, radiant heat and light are combined, and when they fall upon dark surfaces are absorbed together. The quantity of radiant matter, too, emanating from the sun, is incomparably great in reference to anything produced artificially. The solar beam passes through a thin plate of glass without decomposition, and falling upon black surfaces upon the other side, is absorbed by, and heats them: but terrestrial radiant matter, emanating, for instance, from a lamp, or candle, or fire, suffers, in such case, a kind of decomposition; the *light passes* through the glass, but part of the *heat is stopped* in the progress; in the case of the sun's ray, the transmitting glass is scarcely heated; in the other case, the glass becomes hot.

It was formerly supposed that terrestrial heat did *not* pass through

* It has hence been assumed, that the negro must suffer more from heat than the European; but it has been shown by Sir E. Home (*Lectures on Comp. Anatomy*), that the sun's rays are absorbed without ill effect, by the black rete mucosum, whereas they blister and scorch the white.

† Pictet first employed a blackened thermometer as a *photometer*. Leslie concluded, from his photometrical experiments, that the light of the sun possessed

12,000 times the intensity of that of a wax-candle, so that a fragment of the sun, of the size of such a flame, would possess the illuminating power of 12,000 candles. With the same instrument he determined the relative transparency of substances: thus he found, that of 100 rays of light, 80 passed through dry cambric, 93 through wet cambric, 49 through thin paper, 80 through oiled paper, &c.

glass, and that glass screens were as effectual as opaque ones in arresting the heat of the fire ; but this is not so ; the most intense artificial heat and light is probably that produced by charcoal ignited by voltaic electricity, and when a small lens is placed before a brilliant star of fire so obtained, and its focus thrown upon an air-thermometer, an elevation of temperature is always indicated. (BRANDE, *Phil. Trans.*, 1820.) Daniell has shown a similar effect in the rays from incandescent lime. (*Phil. Mag.*, N. S., ii. 59.)

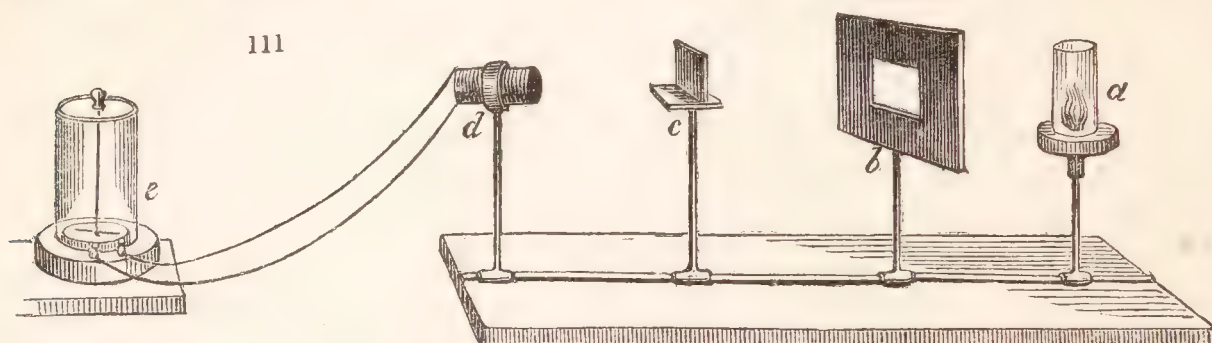
There are other well known instances in which the passage of common radiant heat through glass is evident ; if we stand, for instance, upon the outside of a shop-window when a gas-burner within is suddenly lighted, we perceive the instantaneous impulse of heat upon the face ; and there is no difficulty in causing radiant heat, even of low intensity, to permeate glass and other transparent media in very thin layers. It was formerly assumed that in these cases the direct transmission of the radiant heat was apparent only, and that it, in fact, was absorbed by, and heated the glass, which therefore itself became the radiating surface ; an objection ingeniously answered by Prevost, who transmitted the heat of a flame through a thin sheet of water, issuing from a jet, so that the nature of the medium, as well as its constant motion, prevented all possibility of the transfer of the heat by any other method than direct radiation.

Newton conceived that radiant matter consisted of *particles* emanating from luminous and heated bodies with prodigious velocity ; these particles he imagined might be of different sizes ; the smallest, constituting chemical rays and violet light, being the most refrangible ; the larger ones forming red light and heat, and being the least refrangible ; and some have assumed that the matter emanating from terrestrial bodies might be so constituted as to be arrested by those transparent media which allow a ready passage to solar rays. Newton put the query, "Whether light and common matter are not convertible into each other?" And, if we consider sensible heat in bodies to depend upon vibrations of their particles, a certain intensity of vibration may send off particles into free space ; and particles moving rapidly in right lines, may in losing their own motion, communicate a vibratory motion to the particles of terrestrial bodies." (DAVY'S *Elements*, p. 215.)* The explanation of the phenomena of radiant heat upon the undulatory theory, will be evident from what has been above stated.

But our knowledge respecting the transmission of heat through different media has been lately much extended by the profound and important researches of Melloni. (*Ann. Ch. et Ph.*, liii. and lv. TAYLOR'S *Scientific Memoirs*, i. and iii.) In these inquiries he availed himself of a very delicate thermo-electric pile, in conjunction with an equally sensitive galvanometer, employing these instruments as a means of determining changes of temperature, or as substitutes for the ordinary thermometer ; how they thus act, and the details of their construction, will be explained under the head *Electricity*. The following wood-cut

* The views of Newton in reference to the nature of radiant matter in general, and to the connection of the phenomena of sensible heat, with those of vibrations of the particles of bodies, will be found in the "Queries" attached to his *Optics*, and are quoted at length by Sir Humphrey Davy, in his "*Elements of Chemical Philosophy*."

represents the arrangement of the different parts of the apparatus which he employed: *a* (fig. 111) represents the flame or heated substance. *b* a screen, through the perforation in which the calorific rays pass so as to impinge upon the substance under experiment, placed upon a stand at *c*. *d* is the thermo-electric arrangement connected with the galva-



nometer *e*. By the help of this apparatus Melloni has shown that heat which has passed through one plate of glass becomes less susceptible of absorption in passing through a second. Thus, of 1000 rays of heat from the flame of oil, 451 were intercepted in passing through four plates of glass of equal thickness, of which 381 were intercepted by the first plate, 43 by the second, 18 by the third, and 9 by the fourth. But perhaps the most remarkable of his discoveries is that of the transmission of radiant heat through certain transparent bodies almost without impediment, while others, physically analogous, resist its passage; nor is this passage of heat dependent upon their transparency in regard to light: the latter are *diaphanous*, the former *diathermanous*. He also discovered a remarkable difference in the properties of the rays from different sources of heat: thus, on comparing the transmissive or diathermanous power of the substances enumerated in the following table, (abridged from *Ann. Ch. et Ph.*, LV. 347,) in regard to the rays of an oil flame, of red-hot platinum, of copper heated to 732° , and of a thin copper vessel blackened on the outside and filled with boiling water, he obtained the annexed results:—

NAMES OF THE INTERPOSED SUBSTANCES.	TRANSMISSION OF 100 RAYS OF HEAT FROM			
	Naked oil flame.	Red-hot platinum.	Copper at 732° .	Copper at 212° .
Common thickness = 0.102 inch.				
Rock salt (transparent and colorless)	92	92	92	92
Fluor spar (colorless and transparent)	78	69	42	33
Rocksalt (clouded).....	65	65	65	65
Beryl	54	23	13	0
Fluor spar (greenish and transparent)	46	38	24	20
Iceland spar	39	28	6	0
Mirror glass	39	24	6	0
Rock crystal (colorless)	38	28	6	0
Rock crystal (brownish)	37	28	6	0
Tourmaline (dark green)	18	6	3	0
Citric acid (colorless)	11	2	0	0
Alum (colorless).....	9	2	0	0
Sugar candy (colorless)	8	0	0	0
Fluor spar (green translucent)	8	6	4	3
Pure ice (colorless and transparent).....	6	0	0	0

Rock salt is the only substance whose powers of transmission are the same for heat from all sources and all intensities, 92 per cent. of the incident heat passing through that substance, whether radiating from a bright flame or from the hand: sulphate of copper, on the contrary, not.

withstanding its transparency as regards light, is *athermanous*, or opaque, as regards heat.

The extraordinary properties of rock salt in regard to radiant heat render it invaluable in these researches; it constitutes "the true glass of radiant heat," and may be cut into lenses and prisms, and used for concentrating heat of all intensities, and decomposing it by double refraction, exactly as glass is in regard to solar rays.

Of 100 rays of heat from the same source, successively incident on water, alcohol, ether, bisulphuret of carbon, and chloride of sulphur, the transmitted rays were 11, 15, 21, 63, and 63. The rays transmitted through similar plates of colored glass, were with violet glass 53, with red 47, with yellow 34, with blue 33, and with green 26.

It would further appear from Melloni's experiments, that as there are varieties of light characterized by different colors, so there are different kinds of radiant heat dependent upon the sources whence it emanates. Rays of light which have passed through blue glass, will pass more readily through a second blue glass than through one of a different color; and calorific rays which have passed through water, will pass more readily through a second stratum of water than through other liquids otherwise more diathermanous. Hence it follows that comparatively little additional heat is absorbed either by increasing the number or thickness of screens of the same material.

Heat was first shown to be susceptible of polarization by reflection by Berard; and Professor Forbes (*Phil. Mag.*, 1835,) and Melloni (*Ann. Ch. et Ph.*, LXV. 5,) have shewn that it may be polarized by mica and by tourmaline.

Having stated these facts concerning the receptive and transmitting powers of bodies in regard to radiant heat, we may now turn our attention to their *emissive energies*, and we shall find that those bodies which have their temperatures most easily raised by the action of rays producing heat, are likewise those which are most easily cooled by their own radiation; or which, at the same temperature, emit most calorific rays; in other words, the *receptive* and *emissive* powers of surfaces, in regard to radiant heat, are co-existent and co-equal.

From what is stated above, it will appear that, if we place two similar metallic vessels filled with water before the fire, the surface of one of the vessels being clean and polished, and that of the other covered with a thin coat of lampblack, the former will receive heat much more slowly than the latter: a blackened saucepan set near a clear fire has its contents much sooner heated than a clean and bright one in the same situation.

Let us now reverse the experiment, and fill the blackened and the polished vessel respectively with hot water, and putting a thermometer into each, leave them upon a table at a distance from each other, and not near the fire, and it will be found that the thermometer falls most rapidly in the blackened vessel; that it cools much sooner than the other.

Another way of showing this fact, consists in painting one half of the surface of a convenient tin or pewter vessel with a mixture of lampblack and gum-water, and leaving the other half or side clean and polished; if it then be filled with boiling water, no very delicate instrument is

requisite to prove that heat is thrown "off" much more quickly from the unmetallic than from the metallic surface; for the hand brought near the former feels a much greater impression of heat than when at an equal distance from the latter. If we paste writing-paper, linen, or thin woollen cloth, or flannel, upon one half or side of a canister, and leave the other side clean, a very similar effect will be observed, for those surfaces radiate much more than metals; and, accordingly, a differential thermometer brought near a canister so prepared, will be affected at a much greater distance by the covered than by the clean surface. In one of Count Rumford's experiments he filled two similar brass cylinders with hot water, one of which was tightly covered with linen and the other naked: the covered vessel cooled 10° in $36.5'$, while the naked vessel required $55'$.

The mutual relation of the receptive and emissive powers of bodies in regard to radiant heat is well shown by a form of experiment devised by Professor Ritchie (*R. I. Journal*, v. 305). For the glass bulbs of a differential thermometer he substituted two hollow discs of thin metal plate: the surface of one of these discs was bright, and of the other coated with lampblack. Between these discs he placed a similar one filled with hot water, of which also one of the surfaces was bright and the other coated: when the heated disc was so placed between the thermometric discs that the blackened surface of the one opposed the metallic surface of the other, and *vice versâ*, no effect was produced upon the thermometer; but when the similar surfaces were opposed, namely, black to black, and metal to metal, the thermometer immediately indicated a great access of heat. In the first position the respective actions of the surfaces exactly balanced each other: in the second the good radiator was opposed to the good receiver, and the two bright surfaces to each other, so that everything favoured the effect on one side, and opposed it on the other, and hence the great effect upon the thermometer.

It will be observed that these effects of radiation are singularly opposed to the *conducting* powers of the respective surfaces. If we touch the clean part of the canister it burns us; but we may place the finger with impunity upon the paper or flannel, which, though a good *radiator*, is a bad *conductor* of heat.

The following table of the comparative radiating powers of different substances, is drawn up from Leslie's experiments:—

Lamp black	100	Tarnished lead.....	45
Sealing wax	95	Clean lead	19
Writing paper	98	Polished iron	15
Crown glass	90	Tin plate	
China ink	88	Gold.....	} Polished
Red lead	80	Silver	
Isinglass	80	Copper.....	
Plumbago	75		

It appears, therefore, that those surfaces which are not metallic, such as soot, paper, glass, &c., are much better radiators of heat than tarnished metals, lead, or iron; and that these latter radiate better than the polished metals, which consequently stand at the bottom of the list. It will also be recollected that the above numbers represent the *receptive* as

well as the radiating powers of the respective surfaces. In regard to roughened metallic surfaces, Leslie found their radiating powers much dependent upon the manner in which they had been scratched; when a number of lines were scratched in one direction upon a bright metal, the force of radiation was increased: he then drew the same number of lines, but so that they crossed each other at right angles, and a still greater radiant power was obtained; as if it depended upon the number of points produced.

The different radiating powers of metallic surfaces is stated by Melloni to be connected with differences in their densities. He formed two silver vessels, one of well hammered plate, the other of cast and slowly cooled metal; one side of each was highly polished, and the other scratched with emery-paper in one direction only. On filling them with hot water, he found the following differences:—

Hammered metal polished	= 10°		Cast metal, polished.....	= 13°·7
Ditto scratched	= 18°		Ditto, scratched.....	= 11°·3

The polished surface, therefore, of the cast metal, radiated much better than that of the forged, showing the superiority of inferior density; but with the scratched surfaces, the radiation is in favour of the hammered or denser metal, an effect which Melloni refers to the compression of its surface by the friction of the emery.

Let us now look at some of the economical applications of the facts arising out of the philosophy of radiation.

Before much was known respecting the radiating, and consequent cooling power of different surfaces, it was presumed that vessels of earthenware or porcelain were better calculated to retain heat, than those of metal; it was rightly argued, that the latter were by far the best *conductors* of heat, and it was inferred, therefore, that they would lose heat to the surrounding air more rapidly than bad conductors. Experienced tea-makers, however, always maintained that the best tea was made in a bright silver vessel, and that earthen teapots were of far inferior power; the former were said to *draw* much better than the latter. This opinion we now know is correct, and the obvious reason for the preference is, that the water retains its heat longer in the metal than in the porcelain vessel, and consequently extracts the soluble matter of the tea-leaves more completely.

“Vessels,” says Sir H. Davy, “that are intended to *retain* their heat, should be metallic, and highly polished; and, independent of elegance and delicacy, there is a reason, obvious from the preceding facts, why metallic vessels for the purposes of the table should be kept as bright as possible. Steam or air pipes for warming houses, should be polished in those parts where the heat is not required to be communicated, and covered with some radiating substance, such as lampblack or plumbago, in those rooms which are to be heated by them. Culinary implements should be blackened, and not polished, on those parts which are to *receive* heat. The heated surfaces of fire-places or stoves should not be metallic, but of stony or earthy materials; and in this case, much more heat will be communicated by radiation.”

It is obvious, that whenever radiant heat is to be absorbed, rough unmetallic surfaces should be employed; and these, in the case of

solar rays, may be blackened, in order to render the heat more intense. Brick walls are excellent absorbers and radiators of heat, and when exposed to the sun's rays they become very hot; afterwards, when the sun goes off, they again radiate the heat which they had previously received, and which caused their excess of temperature over the surrounding bodies. Walls against which fruit-trees are planted are sometimes painted black, in order to get the highest possible degree of heat during their exposure to the sun; but it is not found that the fruit is thus improved.

The way in which we receive heat from our ordinary fire-places will now be intelligible, and it will be evident that it is principally by *radiation*, the hot and dilated air making its escape up the chimney, attended by an enormous waste of heat, and consequently also of fuel. The heat which radiates from the glowing coals, and from the heated surfaces about the grate, is projected into the chamber, traversing the air without heating it, and impinging upon the different bodies around, is received by them with different degrees of facility, dependent upon the nature of their surfaces: the carpet, and all similar surfaces absorb the radiant heat with facility; furniture and wooden articles become also heated; and these radiate in their turn, and throw off their excess of heat above that of surrounding bodies. They also warm and dilate the air in contact with them, and thus the heat becomes more or less equally diffused throughout the chamber. Our clothes are also, in general, good absorbers of heat; so is the skin or cuticle; and by the absorption of the radiant heat we get warm on standing before the fire, at least upon that side or part which is exposed to it. This partial reception of heat by which we are burned on one side, while the other may be very cold, is one of the great objections to our common mode of warming apartments; and another is, that in winter, one part of the room is only comfortable, whilst others are disagreeably cold. In rooms heated by throwing into them a current of warm air, such inconveniences are not experienced; but then, unless there is at the same time a thorough ventilation, they produce a sensation of closeness which is unpleasant to those accustomed to open chimneys and fires. A combination of the two systems is the most efficacious and pleasant; warm air, properly and judiciously admitted at the parts of the room furthest from the fire; and an open grate, to assist in warming, and to accomplish a perfect ventilation. Grates or stoves have lately been contrived in which there is an open fire as usual, and which also throw out a stream of warm air, heated by being made to pass from below upwards through a double casing, surrounding all the heated parts of the grate; these stoves, when properly made and applied, are extremely effective and economical.

But it is seldom recollected that all attempts to render any individual apartment in a house uniformly warm, will be frustrated, unless the mass of air in the halls and staircases is also heated; this is most effectually accomplished by a properly-constructed stove upon the basement story, and although the expense of such an arrangement is considerable at first, it will be found, if properly and judiciously made, to effect a material annual saving in fuel. Dr. Arnott's stoves are also excellently adapted to many of these purposes. Whilst upon this subject I may be allowed to remark, that it is to be regretted that architects and builders are in general

inattentive to proper provisions for warming and ventilation, both as concerns dwelling-houses and public edifices.

From what has been elsewhere stated respecting the conducting and carrying powers of bodies, in respect to heat, and from the phenomena of radiation, it is obvious that when a body is allowed to cool in the air, its heat will be carried away, first, by the absolute conducting power of the medium; secondly, by currents established in it, in consequence of change of density; and thirdly by radiation; and that the separate influence of each of these causes must be considered. Supposing, however, a body to be placed in a *perfect vacuum*, its heat would be dissipated by radiation only; to determine, under these circumstances, the rate of cooling, an elaborate inquiry has been undertaken by MM. Dulong and Petit (*Ann. Ch. et Ph.*, vii.); but the details rather belong to physical than chemical science. It appears that bodies cool about twice as fast in the air as in vacuo: Dr. Franklin conceived that a body requiring five minutes in vacuo, would cool through the same number of degrees in air in two minutes. Count Rumford gives the proportions of five minutes and three. But the rate of cooling will much depend upon the relative temperature of the body, and it will lose unequal quantities of heat in equal times, forming, according to Newton, a decreasing geometrical progression. Thus, supposing the temperature of a body to be 1000° above the surrounding medium, and that it were to lose 100° of heat in the first minute, it would lose 1-10th of the remaining 900° in the second minute, (or 90°), and 1-10th of the residual 810° (or 81°) during the third minute, and so on; so that the number of degrees lost during the first five minutes, would be 100, 90, 81, 7.29, and 65.6. This law of cooling, however, though perhaps tolerably correct at low temperatures, becomes liable to much error at high ones, the error increasing as the temperature augments.

The general laws of the radiation of heat which have been deduced from the preceding, and other experimental data, are principally the following:

1. Like all other emanations, its intensity, in a vacuum, varies in the ratio of the inverse square of the distance from the radiating point: in air, and in the various gases, the decrease is somewhat accelerated in consequence of partial absorption.

2. The amount of radiation, or in other words, the rate at which a body parts with its heat, is proportional to the excess of the temperature of the body above that of the medium in which it is placed: it follows, as above stated, from this principle, which was assumed by Newton, that if the times of cooling be taken in an arithmetical progression, the heat will decrease in a geometrical progression; the principle, however, as we have had occasion to remark, is found by experiment only to hold good within a certain range of temperature, not, for instance, exceeding about 50° of Fahrenheit's scale. At the higher temperatures, Dulong and Petit found the rate of cooling to be more rapid than in the ratio just stated.

3. All bodies placed in an inclosed space assume, in time, the temperature of the inclosure.

4. Heat is emitted from every point of the surface of a hot body in all directions; and the intensity of the heating ray is as the sine of the angle which it makes with the surface. This result, which is by no

means obvious, was discovered by Leslie; and its physical cause is, that radiation takes place, not from the surface alone, but from particles situated within a certain minute but sensible depth, which is different for different surfaces.

5. The intensity of radiation varies with the nature of the radiating body and the state of its surface with regard to polish, color, and source of heat: it is greatest for rough surfaces, and least for smooth and polished, and especially for bright metallic surfaces.

The actual velocity of the propagation of radiant heat through space is unknown, but it is probably very great, and not inferior to that of light. (See LESLIE's *Experimental Inquiry*. PREVOST, *Essai sur la Calorique rayonnante*, 1800. FOURIER, *Théorie Analytique de la Chaleur*, 1822. LAPLACE, *Mécanique Céleste*, V. POISSON, *Théorie Mathématique de la Chaleur*, 1835. KELLAND's *Theory of Heat*, 1837. *Reports to the British Association*, 1832, 1835, 1840.)

§ 18. PHOSPHORESCENCE.

THIS term is generally applied to those bodies which shine in the dark, without undergoing combustion, though, in some cases, a low form of combustion goes on at common temperatures, or when substances are only slightly heated, which has occasionally been confounded with the luminosity of phosphorescence. (See a report upon this subject, by Dr. C. Williams, in the *Proceedings of the British Association*, iv. 588.) The products of *combustion* (properly so called), at different temperatures, will be noticed in the sequel. The varieties of *phosphorescence* may be considered under the following heads:—

1. Bodies which become luminous after having been exposed to light, and which are generally called *solar phosphori*.

2. Bodies which become luminous when moderately heated.

3. Bodies of vegetable and animal origin, which are spontaneously luminous at common temperatures.

1. SOLAR PHOSPHORI. The attention of philosophers was first drawn to this curious subject, by an accidental discovery of Vincenzo Cascariolo, a shoemaker of Bologna, who (about the year 1630), being engaged in some alchemical experiments, had occasion to calcine a quantity of a species of native *sulphate of baryta*, found near Bologna, at Monte Paterno. (AIKIN's *Dictionary*, Art. PHOSPHORI.) He observed that, whenever the spar had been sufficiently heated, it acquired the property of shining in the dark after having been exposed to the sun's rays, and that it would even continue thus to emit light for some hours. In consequence of this discovery, the Bolognian spar came into great request among the curious; and the best mode of preparing the *Bolognian phosphorus*, as it was called, became a subject of no small pecuniary importance. The most successful preparers of it were a family of the name of Zagoni, who continued to supply large quantities of it to the curious throughout Europe, and retained their monopoly for many years. Their process is not exactly known; but if the spar be powdered, and made into thin cakes, with mucilage of gum tragacanth, and then carefully calcined in the open fire, and suffered to cool slowly, they will be found to answer the purpose: that is, they will glow for some time in a dark room, after

having been exposed to sunshine. Some management, which can only be learned by practice, is requisite in conducting the calcination. Any variety of native sulphate of baryta will answer for the above preparation, but that which is massive, nearly opaque, and of a lamellar fracture, furnishes the most luminous product.

There are many other substances possessed of properties analogous to those just described. For the discovery of one of these we are indebted to Canton, by whose name it is usually known. *Canton's phosphorus* is made by calcining oyster-shells in the open fire for half an hour; after which the whitest and largest pieces are selected, mixed with about one-third their weight of flowers of sulphur, pressed into a crucible with a closely luted cover, and heated red-hot for an hour. When the crucible has become quite cold, turn out its contents, and select the whitest pieces for use. (*Phil. Trans.*, XLVIII. 337.)

For the following solar phosphorus, we are indebted to Mr. B. Wilson (*On Phosphori*, p. 20) :—"Select a score of oyster-shells, the thicker they are the better; then take most of the flaming coals, but not all of them, off a fire that is burning briskly, strew the shells over the surface, and replace the coals that have been taken off. In about an hour's time take out the calcined shells, observing to break them as little as possible; and after exposing them for a few minutes to the light, they will be found to have acquired a high degree of phosphorescence, glowing in the dark in a very beautiful manner, with most of the prismatic colors. It is not, however, absolutely necessary that the shells should be calcined in the open fire, for if they are heated sufficiently in a close crucible, they will exhibit prismatic colors, chiefly blue and green, though not so bright as by the former method. If the calcination is effected in an iron crucible, all those parts of the shells that have been in contact with the sides of the crucible will glow with a red light. The contact of inflammable matter, and particularly charcoal, with the shells during their calcination, appears eminently to contribute to the brilliancy of the phosphorus. Hence it is that if the shells are calcined in a crucible, in contact with thin plates of steel, (steel being a compound of iron and charcoal,) the phosphorus thus produced will be much more bright, and of more various colors than when plates of iron are employed; and, on the other hand, if flat pieces of charcoal are made use of, the intensity of the colors, especially of the blue, green, and red, is far greater than in those produced by the steel."

Another solar phosphorus is that discovered by Balduin. It is made by saturating diluted nitric acid with chalk, and evaporating to dryness, by which a *nitrate of lime* is obtained. This, when melted at a dull red heat, cools into a compact mass, which has the property of imbibing and emitting light. (*Phil. Trans.*, 1675.)

It has been observed, in regard to these *solar phosphori* in general, that their luminous power is diminished by cold, and increased by heat; that they are more brilliant in dry and warm than in wet and cold weather; that they shine most intensely after exposure to direct sunshine; but that some of them, especially the oyster-shells, exhibit their phosphorescence when carried into a dark place, after mere exposure to ordinary daylight. It is sometimes said, that they absorb the same colored light as that to which they are exposed, and that, if exposed to

red light, they give out red, to green, green light, and so on; but this appears to be a mistake, the colors of the light being white or reddish white, and often prismatic; but independent of the colors of the rays to which they have been exposed. Moonlight is inadequate to render these bodies luminous; but the flash of gunpowder, the light of a bright candle or lamp, or of an electric explosion, suffices to make them shine more or less intensely. The blue end of the spectrum, and blue and violet light are more effective in giving intensity of phosphorescence to these substances, than the green or yellow rays; and red light is almost inefficient.

The above are the most remarkable solar phosphori, but there are several other substances possessed of very similar properties, such as some diamonds, rock-crystal with its surface roughened, certain saline bodies, and writing-paper: these, however, are less powerfully luminous, and require good management to be observed. They should be brought out of the light to the observer, who should be stationed in a small closet, painted black on the inside, and with a black curtain hung up before the door. (BECCARIA, *Acta Bologn.*, 1744—1747, and *Phil. Trans.*, Lxi. 212. See also HEINRICH, *Bib. Univ.*, xv. 247. BECQUEREL and BIOT, *Comptes Rendus*, viii.)

2. PHOSPHORI FROM HEAT. There are many substances which become luminous when moderately heated; that is, at a temperature below a red heat. These differ from the preceding in the circumstance, that, after having been kept at any particular temperature till their luminousness is exhausted, they are incapable of shining again, except at a temperature greater than that to which they were first subjected. The substances belonging to this class are extremely numerous, and an extended series of experiments upon them, by Sir D. Brewster, will be found in the *Edinburgh Philosophical Journal*, I.; but there are only a few which are eminently luminous; of these the compact *phosphate of lime*, found native near Estramadura, in Spain; and certain kinds of *fluor*, or Derbyshire spar, especially the dark blue and slightly fetid variety, are the most remarkable: the former exhibits a beautiful pale-green light, intense enough to be seen in the daytime; and the latter shines with a purple tint; a variety termed, from its shining with a green light, *Chlorophane*, is particularly brilliant and beautiful. The best way of exhibiting them is to heat them in a dark room, in a spoon of platinum, over a spirit-lamp, the light of which is not sufficient materially to interfere with the observance of their phosphorescence. They should be in small fragments, but not too finely powdered. The *fetid carbonate of lime*, called *swinestone*, common near Bristol, several varieties of *calcareous spar*, and of *heavy spar*, and *powdered quartz*, are substances which are also luminous when heated; they may be strewed for this purpose upon a piece of iron which has been heated red-hot, and just ceased to glow. Pearsall has shown that after the luminosity of many of these substances has been destroyed by heat, it may be restored to a certain extent by electrical discharges; and that electricity generally exalts the power, and in some cases confers it where it did not previously exist. Several other curious facts, in reference to this subject, will be found in his papers. (*Roy. Inst. Jour.*, i. 77 and 267.)

The substances which are phosphorescent by heat are also generally

so by *friction*, which is another productive source of luminosity. There are also several bodies which are rendered luminous by passing an electric shock through or over them; such, for instance, as a lump of loaf-sugar, which shines for several seconds afterwards with a beautiful blue light. (SKRIMSHIRE in *Nicholson's Jour.*, xv., xvi., and xix.) Water and several other liquids and saline solutions are said to become luminous under sudden and violent compression; and gaseous bodies, under similar circumstances, are said to exhibit the same phenomenon. In the experiment of suddenly breaking a layer of bladder by the air's pressure, a flash of light is sometimes perceived at the moment of the rupture.

3. SPONTANEOUSLY PHOSPHORESCENT SUBSTANCES. Under this head we may place a variety of *animal substances* which, under certain circumstances, emit light. The flesh of certain fresh and salt-water fish becomes luminous previously to its putrefaction; of these the tench and carp, and the herring and sole, are perhaps the most remarkable; the fish should be gutted and split, and the scales scraped off; if placed in the dark, they are then often observed to shine within twelve or twenty-four hours, the time depending upon the temperature and state of the atmosphere, and probably other causes which have not been determined: this appearance ensues before any bad odor is perceptibly exhaled; and soles are sometimes thus luminous, when perfectly fit for the table. Lobsters and crabs, under similar circumstances, are often rich in phosphorescent matter. It appears, from the experiments of Canton and Hulme (*Phil. Trans.*, vols. lix., xc., and xci.), that sea-fish become luminous in about twelve hours after death, that it increases till putrefaction is evident, and then decreases. Immersion in sea-water does not affect this luminous matter, but the brine is itself rendered luminous: it is extinguished by pure water, and by a variety of substances which act chemically upon the animal matter. The ligamentous parts are more luminous than muscular fibre; especially the eyes. Phosphorescence is rarely observed in the flesh of quadrupeds, and never in that of birds, under any circumstances of decomposition.

There are many *living animals* which have various powers of emitting light. One of these is the *glow-worm*; and there are others which, under certain circumstances, are powerfully phosphorescent. The common *hundred-legged worm*, found under bricks and pots in the garden, exhibits brilliant flashes of light when irritated. The *lantern* and *fire-flies* of warmer climates are also remarkable for their emission of light.

Dr. Macculloch, in his work on the Western Islands of Scotland, and in a paper published in the *Quarterly Journal* (xi. 249), has detailed some valuable facts respecting that beautiful appearance of light in sea-water so well known to those who are conversant with the ocean during the darkness of night; he has shown that the sea is often crowded with worms and insects nearly invisible, and that its luminous property not only bears a relation to the existence and number of these at any time, but may generally be traced to the individuals by which it is caused. One of these luminous animals, described by Captain Home, is figured in the *Quarterly Journal*, N. S., vol. iv., p. 383. (See also C. MATTEUCCI, *sur la Phosphorescence des Vers luisants. Ann. Ch. et Ph.*, Sept., 1843.)

In the *vegetable world* phosphorescence is a less common quality. *Decayed wood*, and occasionally *peat*, have been observed to emit a faint

light; and there are a few flowers, among which may be mentioned the *tuberosa*, *nasturtium*, and *marigold* (*Tropæolum majus*, and *Calendula vulgaris*), which have occasionally been observed to give out brilliant flashes upon a warm summer's evening. The leaves of the *Phytolacca decandra* have also been seen to emit light, and a similar appearance is mentioned by Mr. Mornay, peculiar to the sap of a Brazilian *Euphorbia*. There are certain mosses too, which occasionally phosphoresce; and some species of *Rhizomorpha* have been observed to be luminous in mines.

Certain substances emit light during crystallization: this has been occasionally observed with sulphate of potassa, but the phenomenon, according to H. Rose (*Ann. Ch. et Ph.*, lxi. 288), is most distinctly observed during the crystallization of arsenious acid from its solution in hydrochloric acid. About an ounce of the vitreous acid (not the opaque or pulverulous) should be dissolved in three ounces of hydrochloric acid, diluted by an ounce of water; it should be boiled for about a quarter of an hour, and then suffered to cool very slowly, which is best effected by gradually diminishing the flame of the spirit-lamp used for heating it; in a dark place each crystal that is formed produces a spark of light, and on shaking the flask many crystals are often suddenly deposited, attended by vivid flashes. When the vapor of benzoic acid condenses into crystals flashes of light are also occasionally observed.

We have now enumerated some of the leading cases of what is properly called *phosphorescence*; it appears to consist in an emission of light, independent of ignition or combustion, and referable to a variety of causes, none of which have been very satisfactorily investigated or explained. There are numerous other cases of luminosity referable to changes in the *electric states* of bodies, and which will afterwards be noticed in detail.

§ 19. EFFECTS OF RADIATION IN NATURE.

THE earth, part of the surface of which is daily exposed to the action of the solar beams, will absorb the rays with various degrees of facility depending upon the nature of the surface; and during the night it will again radiate, or throw off a portion of the heat it has so acquired. It has been ascertained that the extent to which this diminution of temperature takes place, is greatly dependent upon the aspect of the sky; when the night is clear, and the heavens cloudless, it goes on more rapidly, and to a much greater extent, than when the sky is overcast and cloudy; and hence it is, that upon clear nights there is a much greater deposition of dew than in cloudy weather. To understand this, it must be recollected, that *dew* is not a kind of fine rain showering down upon the earth from above, but that it depends upon the deposition of moisture contained in the state of vapor in the air, and is, in its formation, precisely similar to what happens when a glass of iced water is brought into a warm room in summer; the coldness of its surface abstracts the heat from the vapor in the air, and causes its condensation in the form of water, which is deposited exactly like dew upon the outside of the vessel*. So the earth, upon a fine cloudless night, in

* This is also the reason why thick and substantial walls in the interior of houses | become damp, and often very wet, in certain states and changes of weather. They

consequence of the accelerated radiation of its own heat, (or according to some, in consequence of the radiation of cold from above,) becomes colder considerably than the superincumbent atmosphere, and therefore the aqueous vapor, more or less of which is always contained in the air, is condensed in the liquid form upon the surface of the ground; and, of course, most abundantly, upon those parts of the surface, which being the best radiators, have their temperatures most depressed. Thus, walking in the garden upon a bright autumnal morning, after a clear night, we observe the dew very unequally deposited: it is commonly most abundant upon the grass-plats, for mown grass is an excellent radiator; it becomes, therefore, colder than the adjacent gravel-walks, upon which the dew is less abundant. If we place a thermometer upon the grass, and another upon the gravel, we shall find the former sink several degrees below the latter; and under circumstances favorable to the deposition of the dew, the earth's surface will always be found colder than the air above it. A thermometer on the grass has been observed, under such circumstances, to fall as much as from twenty to thirty degrees below one suspended some feet above it. The consequence is, that the lower strata of the atmosphere in contact with the cold surface of the earth, are considerably colder than the higher parts; and if the air is tranquil, will remain so for some time, especially in *hollows*, and other places protected from currents, and where the warm and the cold air are not therefore mixed by mechanical agitation. Hence it is that delicate plants often suffer more in situations apparently protected, than in those which are open and exposed, and where the cold air has not such a chance of lying quiet upon the surface. (WELLS, *on Dew*. DANIELL'S *Meteorological Essays*.)

All good radiators, exposed upon the earth's surface, will become colder than bad ones; if, therefore, we place upon an exposed gravel-walk a piece of flannel and a piece of tin-foil, the former will have abundance of dew thrown down upon it, and the latter none; and, in reference to this fact, it is curious to observe the influence of the natural textures and surfaces of foliage. Smooth, varnished leaves have no dew deposited upon them, under circumstances in which there is an abundant deposition upon rough and downy leaves; the former, therefore, seldom suffer from this cause of cold, but the latter are often frost-nipped.

The remarkable influence of clouds in preventing radiation, seems first to have been noticed by Dr. Wells, whose *Essay on Dew* deserves the attentive perusal of all who are interested in this part of meteorology. He found that, if the night, at first clear, becomes cloudy, the temperature of the grass always rises, independent of any changes of calmness, and nearly so of change of atmospheric temperature. Upon one such night the grass, after having been *twelve* degrees colder than the air, became only *two* degrees colder, the temperature of the atmosphere remaining stationary; and, on another occasion, the temperature of the

are so massive as to retain an acquired temperature for a long time, and during a winter's frost become cold throughout; upon a sudden thaw attended by a very humid state of atmosphere, the vapor or

moisture of the air is condensed in the liquid state upon these cold surfaces, because they abstract its heat, and consequently cause it to run down in the form of water.

grass rose *fifteen* degrees, while the air only sustained an increase of *three and a half*. Any protection interposed between the earth and sky, prevents radiation, in the same way as a cloud. If we place four poles in the ground, and stretch a mat or canvass upon them, the plot underneath will be effectually preserved from those changes of temperature referable to the escape of radiant heat from the surface, (or, to the reception of radiant cold from above.) In this way gardeners protect young and tender plants; though it is obvious that any general changes, dependent merely upon atmospheric temperature, would not be interfered with, nor the cold kept off by such a contrivance.

Radiation, therefore, is constantly going on from the earth towards the regions above. If we place the bulb of a delicate thermometer, especially if it be covered with some good radiating substance, in the focus of a concave metallic mirror turned towards the clear sky, it will indicate cold: this was referred by Leslie to radiation of cold from the regions of space; and thus he employed a differential air-thermometer in the construction of his *Æthrioscope* (see *Encyc. Brit.*, Art. CLIMATE,) to indicate, as he terms it, "*the cold pulses emanating from the sky*," or, as others have expressed it, to give a comparative idea of radiation proceeding from the surface of the earth towards the region of perpetual congelation in the atmosphere. "The thermometer is protected by its position from the radiation of surrounding objects, and its own radiant heat is projected towards the clear space, or falling upon the concave surface of the mirror, is reflected in parallel lines in the same direction. This effect is produced even while the sun is above the horizon, provided the mirror be turned from the direct rays of that luminary; and at night a depression of 17° below the temperature of the air and surrounding objects may commonly be produced. Perfect stillness of the atmosphere is necessary, and perfect transparency also, for otherwise the balance of temperature is soon restored by convection, and the slightest mist destroys the effect by a counter-radiation." (DANIELL, *Introd.* § 275.)

In the eighty-third volume of the *Philosophical Transactions*, Mr. Williams has described the mode of obtaining ice in Bengal, where the atmospheric temperature never falls to the freezing-point. It is evidently chiefly effected by radiation from the surface of shallow pans of water (and water is a good radiator), which are placed upon dry stubble in open situations; calm, serene, and cloudless nights are most favorable to the purpose; and thin crusts of ice are thus frequently obtained. In such cases the production of cold has sometimes been referred to evaporation, but that this is not the cause of the diminution of temperature, in the present instance, is proved by the peculiar circumstances requisite for the success of the operation being entirely independent of it.

"Land and sea breezes are certain periodical winds common to most sea-coasts within the tropics, but by no means confined to those regions. It is observed that a few hours after sunrise a breeze springs up at sea, and blows directly on shore, and that its intensity increases as the day advances, and declines, and gradually expires, near sunset. Shortly afterwards a wind arises in exactly the opposite direction, namely, from the land towards the sea, lasts the whole of the night, and only ceases with the re-appearance of the sun. It is easy to give an explanation of these effects. When the sun shines at once upon the surface of the

earth and that of the sea, the two become unequally heated from their different absorbing power; the land becomes much the warmest. The air over the heated surface of the ground being expanded by heat, rises, and has its place supplied by the colder air flowing from the sea, producing the sea-breeze. When the sun sets both sea and land begin to cool by radiation: the rate of cooling of the latter will, however, far exceed that of the former, and its temperature will rapidly fall. The air above becoming cool and condensed, flows outwards, in obedience to the laws of fluid pressure, and displaces the warmer air of the ocean. In this manner, by an interchange of air between sea and land, the otherwise oppressive heat is moderated, to the great advantage of those who inhabit such localities. The land and sea breezes extend to a small distance only from shore, but afford, notwithstanding, essential aid to coasting navigation, since vessels on either tack enjoy a fair wind during the greater part both of day and night." (FOWNES, *Manual*, 65.)

§ 20. OF IGNITION AND COMBUSTION.

It will be evident, from the contents of the few preceding pages, that there is a connection between light and heat, and that they are mutually disposed to produce each other; indeed, they are probably convertible into each other; but these, and other mysterious relations between them, are as yet very imperfectly understood*.

By the terms *ignition*, and *incandescence*, we express a property which bodies possess of giving out light, whenever their temperatures are raised up to a certain high point. The quantity of light thus emitted increases with their temperature: at first it is dim and feeble; then it becomes dingy red, and the bodies are said to be *red-hot*; then bright red, commonly called a *cherry-red* heat; then, as the temperature increases, the body becomes of an *orange* or *yellow* tint, and at length acquires such brilliancy as to be painful to the eye; the latter is usually termed *white heat*.

Various experiments have been instituted to determine the temperature at which bodies become visibly red-hot; this, in a dark place, certainly exceeds six hundred and sixty degrees of Fahrenheit's scale, for at that temperature mercury boils, and it is not, in the least degree, luminous. Sir H. Davy's experiments place the degree of incipient luminosity in a dark place at about 810° . A dull red, visible in daylight,

* A supposed exception to the relationship between heat and light, is furnished by an examination of the *lunar rays*, which, though concentrated by the most powerful lenses, are incapable of affecting very delicate thermometers. De la Hire collected the rays of the full moon when in the meridian, by a lens thirty-five inches in diameter, and threw them upon the bulb of a very sensible air-thermometer, but they produced no effect, though they were thus concentrated 306 times. It is not, however, surprising that the moon-beam should be thus inefficient, when we consider the

extreme feebleness of its illuminating power, as compared with a solar ray of the same size; the light of the latter being at least 300,000 times greater than that of the former. It appears probable, therefore, that the properties of the moonbeam are to be referred to its *feebleness*, as compared with that of the sun, though there may be some peculiarity in its nature, or some power in the surface of the moon of retaining the heat, whilst it emits the light received from the sun. It has even been supposed that the moon may radiate cold.

is probably equal to about 1000° , a full red heat to 1200° , an *orange heat* to 1700° , and a white heat to 3000° . According to Daniell, the highest temperature of a good wind furnace (a high white heat) is about equal to 3300° Fahrenheit.

These observations of course only apply to bodies capable of sustaining high temperatures without changing their state, or undergoing decomposition, most substances being either dissipated or destroyed before they attain the requisite temperature for ignition; or, if heated in the air, *inflaming* and undergoing *combustion*.

In all the ordinary cases of combustion air is present, and the phenomena presented by the burning body are referable to the chemical action which ensues, at high temperatures, between it and one of the component parts of the air, called *oxygen*, which, being invisible, long escaped observation as an important agent in the process, and of which we shall have to speak at length hereafter.

The *temperatures* at which bodies burn or inflame in the air are extremely various; some take fire under all circumstances the moment they are exposed to it: others require their temperatures to be more or less elevated; and some refuse to burn under any circumstances. Thus we speak of *combustible* and *incombustible*, or *inflammable* and *uninflammable* bodies; and we call the oxygen of the atmosphere, and such other bodies as are possessed of similar powers, *supporters of combustion*. All common cases of combustion, then, taking place in the atmosphere, depend upon the union of the combustible with oxygen; between these bodies there necessarily exists a strong chemical attraction, and of this, one of the results is the *evolution of heat and light*.

The result of the union of the combustible with the supporter, is called the *product of combustion*; it is very commonly gas or vapor, and eludes ordinary observation: thus, the enormous quantity of coal daily consumed as common fuel, combines with the oxygen of the air, and forms several products, of which the principal are *carbonic acid gas* and *steam*; and these pass off by the chimney, and are dissipated in an invisible state through the immense mass of the atmosphere. The *incombustible* matter contained in the coal forms *ashes*; or, mixing with a part of the coal, renders it difficult of combustion, as we see in *cinders*, which, when more or less fused, are called *clinkers*.

But the product of combustion is often a *solid* body; thus, if we throw a piece of the metal *zinc* into the fire, or heat it red-hot in a crucible, it burns with a very vivid flame, and a quantity of a solid white substance is produced, which is a compound of the metal and the oxygen of the air, and is, therefore, called *oxide of zinc*.

Nothing is more common than to speak of the *destruction* of bodies by combustion; but the term is in so far improper, inasmuch as *matter is indestructible*; and when we seem to destroy a coal by burning it, we, in fact, only cause it to enter into new combinations; and the carbon which it chiefly consists of, although it apparently disappears, has only entered into a new combination, which may be found escaping from the chimney in the invisible state of air or gas, but from which the solid carbon may again be obtained by certain chemical operations.

Such are the general results of combustion: they have here been

adverted to in order to explain the nature of *flame*, a subject which has been studied with much attention and curious results by several eminent chemists.

It has often been doubted whether pure gaseous matter is, under any circumstances, susceptible of becoming luminous; certain it is, that its temperature may be elevated far beyond that which is required to ignite solid bodies, and it yet remains invisible. By passing air over heated surfaces, its temperature has been so far elevated as to render metallic wires red-hot, yet was the air itself not at all luminous. Of this a good instance is afforded by the air that issues from the lamp-glass of an Argand gas-burner, which, though not luminous, will heat a fine wire red, or even white hot, held some inches above it. *Flame*, however, may, in general, be regarded as *luminous gaseous matter*, and its *temperature* is under certain circumstances very intense, even where the *light* which it emits is excessively feeble. Perhaps the purest form of flame which we can exhibit is that of hydrogen gas; its *light* is so feeble as scarcely to be visible in broad daylight; yet its *temperature* is very high, as may be shown by holding a fine platinum wire in it, which immediately becomes *white-hot*: the other metals, under similar circumstances, are generally melted or burned.

Upon what, then, does the *luminosity* of a flame, which renders it valuable as a source of artificial light, depend? *Principally upon solid matter diffused through it, and ignited by it.* In the experiment just cited, the flame of the hydrogen is rendered luminous by the wire; and if we blow any substance through it in fine dust, its brightness will be proportionately increased, though the solid matter be not itself inflammable; as, for instance, if we sift a little lime or magnesia into or through it.

The extent to which the light may be increased is also well illustrated by the ignition of lime in the oxyhydrogen blowpipe, as suggested by Drummond (*Phil. Trans.*, 1826, p. 324), and as since used for the illumination of the solar microscope: and that particles of lime, raised to this high temperature, occasion the intensity of the light, is shown by the roof of the lantern being covered by a sublimate of lime. There can be little doubt that the brilliancy of the voltaic discharge between points of charcoal is partly referable also to the formation and ignition of volatilized carbon. There are few instances of a more luminous flame than that of phosphorus, in which the great evolution of light depends upon the ignition of the produced phosphoric acid, and if this acid (forming the smoke of phosphorus) be led by a tube into the flames of alcohol or of hydrogen, it greatly increases their luminosity.

In the flame of tallow, wax, oil, and coal-gas, the brilliancy of the light is chiefly owing to very finely-divided charcoal, which is blended with and burned in the flame, and which, if in too large quantity, causes the flame to smoke, as we see especially in ill-made tallow-candles, which, notwithstanding frequent snuffing, throw off a quantity of soot into the surrounding atmosphere, creating a disagreeable suffocating smell, and blackening the walls and ceilings of our apartments. When coal-gas is deficient in carbon and consequently in luminosity, giving what is called a thin and poor flame, it may be improved by passing it over a surface of naphtha, the vapor of which being taken up, and very rich in carbon,

greatly increases the illuminating power. Lowe's *patent naphthalizer* acts upon this principle.

Such, then, appears to be the source of the *light* of flames*; but there are some other curious particulars respecting their construction, which require more full explanation. In a common candle, the wax or tallow is drawn into the burning wick by capillary attraction, and is there converted into vapor, which ascends in the form of a conical column, and has its temperature sufficiently elevated to cause it to combine with the oxygen of the surrounding atmosphere with a temperature equivalent to a white heat. But this combustion is *superficial* only, the flame being a thin film of white-hot vapor, enclosing an interior portion, which cannot burn for want of oxygen. That this is the case, is easily shown, by bringing down a piece of thin glass upon the flame of a candle so as to cause a transverse section of the flame. We shall then observe a *ring*

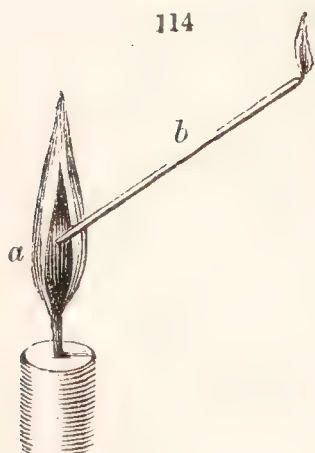
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of light surrounding the interior dark part of the cone (fig. 112,) and the vertical section of the flame will put on an appearance resembling fig. 113. To prove that *the interior dark part consists of inflammable gaseous matter*, we may insert one end of a small glass tube into the dark central portion of the flame of a large candle, and the interior gas will then make its escape through it, and may be lighted at the other end of the tube, so as to form a second flame. Fig. 114, *a*, shows a section of the flame; *b* the glass tube held in an inclined position in the central part of the flame; *c* the inflammable gas kindled at its extremity.



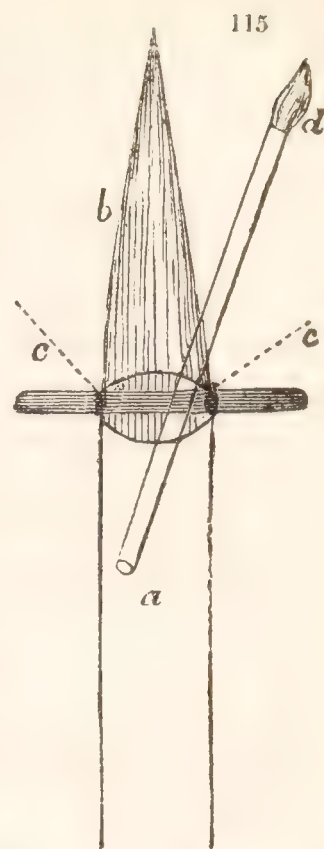
It is in consequence of this structure of flame that we so materially increase its heat, by propelling a current of air through it by the *blowpipe*, or by supplying its interior with oxygen, as in the gas jet suggested by Daniell. (*Phil. Mag.*, 3rd Ser., II., 57.) The perfection of the *Argand burner* is also referable to a similar cause.

These peculiarities become more evident in larger flames: so if in a steady atmosphere we inflame some ether or alcohol in a small capsule, we may introduce phosphorus or gunpowder into the centre of it, and they will not be inflamed.

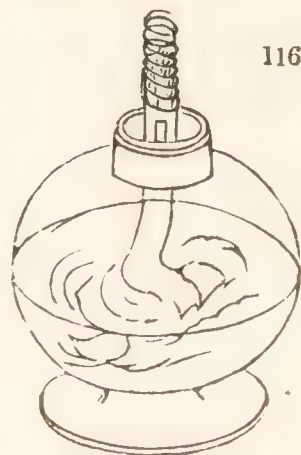
* For all common purposes of illumination it is essential that the constitution of the light of flames should resemble that of the sun, and, like it, consist of a due admixture of the primary colors; it is seldom, however, that artificial light is perfect in this respect, and accordingly it is not suited to the correct and perfect display of colors, and when viewed through a prism generally shows a predominance of some one tint. The influence of light of *one color* upon external objects is seen by viewing them through colored glasses, or more perfectly by illuminating them by a *monochromatic flame*. We obtain an effect of this kind by a lamp

fed with spirit of wine burning in a wick impregnated with common salt, and which, as it produces little else than yellow light, has been called a *monochromatic lamp*; it shows no perfect color except yellow, and furnishes a curious analysis of such compound colors as contain yellow by converting them to that tint; all other colors appear very dingy, and nearly black. The brilliant red of cinnabar, as in sealing-wax, and of iodide of mercury, appear pale yellow; that of cochineal, as in lake and red morocco, looks black; so also do the brilliant blues of smalt and ultramarine. See Sir D. BREWSTER'S *Letters on Natural Magic*, p. 107.

A large jet of gas issuing from the top of a lamp glass, may, with a little management, be so inflamed as not to pass down to the orifice of the burner, and it then forms a hollow cone of flame; a small rod of wood, such as a pencil, or a piece of twisted paper, may then be placed across the flame, and it will only be charred or burned at the luminous surface, and not at all affected in the centre. *a* represents the lamp-glass, through which the current of gas is passing; *b* the cone of flame at its mouth: a piece of wood laid across it is singed at *c*; and by the tube, *d*, gas may be drawn out of the interior, and inflamed at its other extremity.



There are several substances which burn at lower temperatures than required for the production of flame. We often see the coals in a common fire glowing at a dull red heat, but not hot enough to inflame the smoke, or inflammable gas and vapor that passes over them, which, however, may be immediately effected by a piece of flaming paper, or by stirring the fire, which not only accelerates the combustion, but mixes air with the vapor, so as to render it more easily inflamed. The long-continued glowing of the wick of a green wax taper (colored by verdigris) is another case of combustion going on at a temperature below that of flame; so is the luminosity of a stick of phosphorus exposed to the air. The phenomena attendant upon such states of combustion are highly curious: when, for instance, spirit of wine is burned *with flame* in the usual way, carbonic acid and water are the products of its combustion; but when burned *without flame*, it produces aldehydic and acetic acid. The mode of effecting this *slow combustion* is sufficiently simple. A small spiral coil of fine platinum wire is placed upon the wick of a spirit-lamp, and allowed to project about a fourth of an inch above it, as represented in fig. 116. The lamp is then lighted, and suffered to burn for a few seconds, when the flame is put out by an extinguisher, which, however, must be *instantaneously* removed. In this way the coil of wire retains heat enough to carry on the *slow combustion* of the alcoholic vapor, and it continues to glow with a red heat as long as spirit remains in the lamp, and to produce the peculiar products just mentioned: in this way of proceeding, the heat never becomes intense enough to cause the inflammable vapor to burn with flame.



There is another, and a very instructive way of making a similar experiment, which consists in pouring a teaspoonful of ether into a tall ale-glass, or small jar of the form represented in fig. 117, and then suspending in it a coil of fine platinum wire, previously heated by holding it for a minute in the flame of a spirit-lamp. The wire being now immersed nearly red-hot into the mixture of atmospheric air and

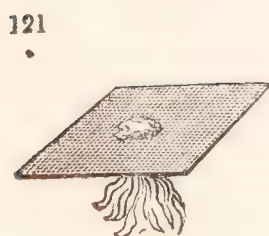
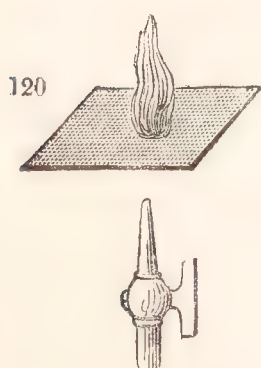
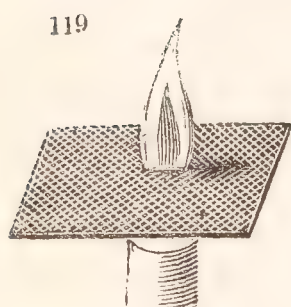
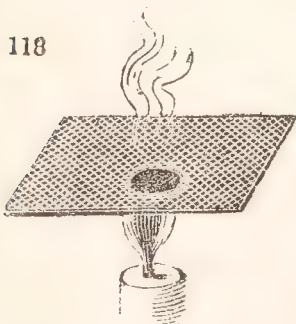


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ethereal vapor, *glows with a red heat, causing the slow combustion of the vapor*. It often happens that a part of the wire becomes *white-hot*, and in that case *flame* is produced, and the ether burns with its usual products; but so long as the wire continues only red-hot, no inflammation ensues*.

It follows then, *that flame requires a very high temperature for its existence*; and consequently, that if we can devise any mode of *cooling* it, it will be *extinguished*. A very small flame, for instance, is extinguished by bringing a large mass of metal near it, or by carefully surrounding it by a coil of wire; the metal abstracts its heat (*Phil. Trans.*, 1817, p. 70). But by far the most interesting experiments upon this subject are made by help of copper, brass, or iron wire-gauze, which may be obtained of different degrees of fineness, and with which the following illustrative experiments are easily shown.

Procure a piece of this gauze about nine inches square, and of such fineness as to have about thirty meshes in the square inch: bring it gradually down upon the flame of a large and steadily burning wax-candle, and the appearances represented in fig. 118 will be produced. The flame will be cut off where it touches the gauze, and we have a good opportunity of observing the exterior luminous circle described above (fig. 112). In this case the inflammable matter of the flame (in the form of smoke) passes through the wire-gauze; but, in its passage, it is so far *cooled* as to be *extinguished*, and the *flame* is thus prevented from traversing the wire-gauze. If we now bring a lighted taper to the upper side of the wire-gauze, the gas or smoke will be kindled, and the flame continue to burn uninterruptedly, as in fig. 119. These phenomena are more conveniently and strikingly exhibited by means of a gas-flame, issuing under low pressure from a single jet; if the wire-gauze be placed across the jet of uninflamed gas, the upper portion may be kindled and will continue to burn upon the gauze, which prevents the descent of the flame so as to kindle its lower half, as represented in fig. 120. The result of this experiment may, as it were, be inverted by placing a small piece of camphor in the centre of a piece of wire-gauze, as in fig. 121, and applying a flame to its *lower* surface. The vapor of the camphor, which is very inflammable, then burns with a bright flame upon the lower surface only of the gauze, and cannot pass upwards through it, in consequence of its cooling power; so that the camphor itself lies upon the surface of the gauze, in an uninflamed state,



* These curious phenomena, discovered by Sir H. Davy in his researches on flame, have led to more extended inquiries respecting the influence of contact, or catalytic action upon chemical combination and decomposition, by Dobereiner, Dulong and

Thenard, Mitscherlich, Kühlman, T. de Saussure, Faraday and others, which will afterwards be noticed more in detail. (See also REISET and MILLON, *Ann. Ch. et Ph.*, July, 1843.)

though sufficiently heated to furnish inflammable vapor for the sustenance of the flame beneath. If the meshes of the wire-gauze used in these experiments be not sufficiently small, or if the wire becomes intensely heated, the flame will pass in either instance; because the cooling power is in the one case prevented by the largeness of the apertures, and in the other, by the high temperature of the wire.

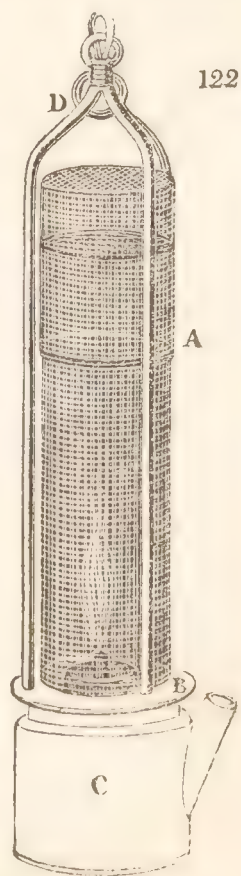
The power, therefore, of the metallic tissue thus to intercept or extinguish flame will depend upon the heat required to produce the combustion, as compared with that acquired by the tissue; and the flame of the most inflammable substances, and of those that produce most heat in combustion, will pass through a metallic tissue that will intercept the flame of less inflammable substances, or those that produce little heat in combustion; so that different flames will pass through at different degrees of temperature. The cooling power of the wire-gauze is referable to its excellent conducting power for heat; it also, by use, becomes a powerful radiator of heat.

These, and many other interesting investigations connected with the subject of flame, we owe to Sir H. Davy, who most ingeniously applied them in the construction of his *miner's safety-lamp*.

Coal-mines are often infested by a species of inflammable gas (carburetted hydrogen), known under the name of *fire-damp*, which, when mingled in certain proportions with atmospheric air, forms a mixture which explodes upon the contact of flame. Attempts had been made to light such mines so as to avoid explosion, but none were effectual; at length Davy constructed a lamp upon the principles explained, which has been used with safety and success.

It is obvious, that if we place a lighted lamp or candle within a perfect cage of wire-gauze, no flame will be able to penetrate *from within* to the surrounding medium, in consequence of the cooling power of the metallic tissue. The annexed figure (122) represents a lamp constructed upon such principles. A is a cylinder of wire-gauze, with a double top, carefully fastened, by doubling over, to the brass rim B, which screws on to the lamp c. The whole is protected and rendered convenient for carrying, by the frame and ring D. If the cylinder be of twilled wire-gauze, the wire should be at least of the thickness of one-fortieth of an inch, and of iron or copper, and 30 in the warp, and 16 or 18 in the weft, to the square inch. If of plain wire-gauze, the wire should not be less than one-sixtieth of an inch in thickness, and from 28 to 30 both warp and woof. (DAVY on the *Safety-lamp*.)

The operation of this lamp may be shown by suspending it in a glass jar, and then admitting a sufficient stream of coal-gas to render the inclosed atmosphere explosive: or, what answers nearly as well, by immersing it into a jar at the bottom of which is a little ether, and which supplies, by its vapor, an inflammable atmosphere. The flame of the lamp first enlarges, and is then extinguished, the whole of the cage being filled with a lambent blue light; on turning off the supply of gas, or gently blowing the ethereal vapor out of the



vessel, this appearance gradually ceases, and the wick becomes rekindled when the atmosphere returns to its natural state*.

As the *safety* of these lamps entirely depends upon the perfect state of the wire-gauze, and upon the non-existence of any aperture or channel sufficiently large to admit the passage of flame, they should, when in use in a coal-mine, be inspected daily. In gas-manufactories, spirit-warehouses, and in all cases where inflammable vapors or gases are likely to be generated, as in the examination of foul sewers and drains, it is obvious that these lamps are importantly applicable†.

* In a subsequent communication to the Royal Society, Sir H. Davy suggested, as improving the safety lamp, the introduction of a coil of platinum wire into the cage: "By hanging some coils of fine wire of platinum, or a fine sheet of platinum or palladium, above the wick of his lamp in the wire-gauze cylinder, the coal miner, there is every reason to believe, will be supplied with light in mixtures of fire-damp, no longer explosive; and should his flame be extinguished by the quantity of fire damp, the glow of the metal will continue to guide him, and by placing the lamp in different parts of the gallery, the relative brightness of the wire will show the state of the atmosphere in these parts. Nor can there be any danger with respect to respiration whenever the wire continues ignited, for even this phenomenon ceases when the foul air forms about two-fifths of the volume of the atmosphere."

"I introduced into a wire-gauze safety-lamp, a small cage made of fine wire of platinum one-seventieth of an inch in thickness, and fixed it by means of a thick wire of platinum about two inches above the wick, which was lighted. I placed the whole apparatus in a large receiver, in which, by means of a gas-holder, the air could be contaminated to any extent with coal-gas. As soon as there was a slight admixture of coal-gas the platinum became ignited; the ignition continued to increase till the flame of the wick was extinguished, and till the whole cylinder became filled with flame; it then diminished. When the quantity of coal-gas was increased so as to extinguish the flame, at the moment of the extinction the cage of platinum became white hot, and presented a most brilliant light. By increasing the quantity of the coal-gas still further, the ignition of the platinum became less vivid. When its light was barely sensible, small quantities of

air were admitted, and its heat speedily increased; and by regulating the admission of coal-gas and air, it again became white-hot, and soon after lighted the flame in the cylinder, which, as usual, by the addition of more atmospheric air, rekindled the flame of the wick." (*Phil. Trans.*, 1817, p. 81.)

† It has been shown, that by throwing a strong jet of coal-gas and air, in explosive proportions, upon the wire-gauze of these lamps, the flame occasionally passes, and this circumstance has been urged as a new experiment, proving the inefficiency of Sir Humphry's safety-lamp; but all practical and unprejudiced experience shows, that when carefully attended to, and used with common caution (which unfortunately is not always the case), they are perfect and efficient safeguards. That Sir Humphrey was aware of the possibility of causing the flame to pass is obvious from the following passages of his essay:—

"Single iron wire-gauze of the kind used in the common miner's lamp, is impermeable to the flame of all currents of fire-damp, *as long as it is not heated above redness*; but if the iron wire be made to burn, of course it can be no longer safe; and though such a circumstance can perhaps never happen in a colliery, yet it ought to be known and guarded against."

"If a workman, having only a common single lamp, finds the temperature of the wire increasing rapidly in an explosive mixture near a blower, he can easily diminish the heat by turning his back upon the current; and keeping it from playing upon the lamp, by means of his clothes or his body; or by bringing the lamp nearer the orifice from which the fire-damp issues, he may extinguish it: and there never can be any occasion for him to place his lamp in the exact *point* where two currents, one of fresh air and one of fire-damp, meet each other."

CHAPTER III.

CHEMICAL ATTRACTION, OR AFFINITY.

IN a former chapter we have considered *attraction* as disposing the *similar* particles of bodies to adhere, so as to form masses or *aggregates*; and, in many instances, to arrange themselves according to peculiar laws, and to assume regular geometrical figures. We then proceeded to show that *heat*, or *calorific repulsion*, was a power opposed to *aggregation*, tending to separate the particles of matter, and in many ways connected with those extraordinary phenomena which have been referred to *ethereal matter*, and under which we were led to speak of *light* and *radiant heat*. We are now to give an outline of the extensive changes which result from certain attractive powers, appertaining to *dissimilar* particles of matter, and sometimes therefore called *heterogeneous*, in opposition to *homogeneous*, *attraction*: they are usually comprehended under the term *chemical affinity*.

§ 1. GENERAL RESULTS OF CHEMICAL ATTRACTION.

A GOOD instance of *chemical attraction* is afforded by the mutual action of *copper* and *sulphur*. If 16 parts of sulphur broken into small fragments be mixed in a glass flask with 60 parts of copper filings, or turnings, no action ensues; they may be triturated together, but still remain a mere *mixture* of sulphur and copper; but, if heat be applied, so as to fuse and vaporise the sulphur, the copper presently begins to *combine* with it; heat and light are evolved, the copper glowing and burning in the sulphur vapor; and a brittle black compound, quite unlike sulphur or copper, namely, a *sulphuret of copper*, is the result. This simple experiment furnishes the following facts for consideration. First, it shows that mechanical aggregation is opposed in this case to chemical action, and that the sulphur and copper do not combine, till the aggregation of the former is diminished or overcome by heat. 2nd. That chemical action is here attended by combustion. 3rd. That the product has properties essentially different from those of its component parts. 4th, That sulphur and copper combine in certain proportions only; certain definite quantities of sulphur and copper being required to form the *sulphuret*.

We may first observe, that *chemical action* is promoted by whatever tends to diminish aggregation or to disintegrate and separate the particles of matter. In the preceding case, this is effected by *heat*; although it be true, as we shall afterwards find, that *electrical powers* may thus be exalted and called into action. It is this property or effect of heat, that renders it so essential an agent in many chemical operations, both upon the large and small scale.

Pulverization is a usual method of diminishing aggregation, in order to facilitate chemical action: a piece of marble is a long time dissolving in dilute hydrochloric acid, and the evolution of its carbonic acid is slow; reduced to powder, it is rapidly decomposed and dissolved. The influence

of aggregation as opposing solvent power and chemical action, is strikingly illustrated by certain forms of alumina; the sapphire and corundum, which are dense and crystalline forms of alumina, resist the action of all acids and alkalis, whereas finely divided and freshly precipitated alumina is extremely soluble. Chlorine has little action upon a lump of metallic antimony, but *powdered* antimony thrown into the gas immediately burns, and produces a *chloride of antimony*. The relative combustibilities of the varieties of carbon furnish good illustrations of the influence of cohesion, from the easily combustible tinder to the difficultly combustible diamond. Iron in a state of extreme division is spontaneously combustible, as when reduced by heating its finely powdered oxide in a current of hydrogen gas. Copper, as obtained in fine powder by precipitation from its solution upon a plate of iron, easily burns when gently heated. Lead, in its ordinary state, is scarcely acted upon by the air at common temperatures; but if the salt called *tartrate of lead* be heated red-hot, in a small tube or phial, the black matter which is obtained contains the *lead in a state of very minute mechanical division*, and in this state it takes fire upon exposure to air.

Another mode of diminishing aggregation, and thereby promoting chemical action, is *solution*, the importance of which, as a prelude to the process of crystallization, has already been noticed: its effects are shown by pouring water upon the mixture of tartaric acid and bicarbonate of soda, commonly termed *effervescent* or *sodaic powders*; the materials, when dry, have no mutual action, but, when dissolved in water, the acid immediately decomposes the carbonate. Hence arose the old, though not perfectly correct, chemical axiom, "*Corpora non agunt nisi sint soluta.*"

There are some cases of chemical attraction, promoted apparently by peculiar states of the *surfaces* of bodies, which are of an extraordinary nature, and not easily explained: such are the action of certain porous bodies, and of perfectly clean, or finely divided (spongy) platinum upon certain gaseous mixtures. If a strip of perfectly clean platinum-foil be introduced into a tube containing two volumes of hydrogen and one of oxygen, over clean water, the gases presently begin to combine, and gradually evolve so much heat as ultimately to render the platinum red-hot, and produce explosion. "The force of adhesion of the gas to the metal suspends, upon its surface, the self-repulsive force of the similar particles of each gas, and brings them within the influence of the mutual affinity of their dissimilar particles: the combination thus commenced, proceeds with greater activity as the affinity becomes exalted by heat." (DANIELL.) When the platinum is in a pulverulent or porous state, its influence is greatly increased. (See *Hydrogen* and *Platinum*; also the preceding illustrations of combustion without flame.)

The evolution of heat and light, attending chemical action, is especially observed where the mutual affinities are intense, or where combination is rapid, and the electrical states of the acting bodies are eminently opposed. That it is not always explicable upon the theory of latent heat, or connected with increase of density, is evident from the numerous cases of an opposite nature in which it occurs, as for instance, in the ex-

plosion of fulminating mercury, and the expansion (attended by decomposition) of the oxide of chlorine. Nor does it appear that any one kind of matter is essential to *combustion*: it is a universal effect of intense chemical action, and proportionate to its rapidity: this is well illustrated in the *slow* and *rapid* combustion of phosphorus; the former exhibits a pale blue light, visible only in the dark, and attended by trifling elevation of temperature; the latter is brilliant in the extreme. When a candle burns, the substances of which it is composed are entering into chemical combination with the oxygen of the surrounding atmosphere; so also with respect to the coals consumed in our fires; and in both cases we observe the combustibles gradually losing their solid form, and acquiring an invisible aëriform state; dissolving, as it were, in the air, and disappearing. If we apply a spark to a small heap of gunpowder, it is instantly dissipated in the gaseous form, and a bright flame ensues. In these cases it will always be remembered that there is no *destruction of matter*, but that the charcoal and other substances, composing the candle, the coal, and the gunpowder, have merely entered into new chemical arrangements, and are to be found, as we shall afterwards particularly show, in the *products of combustion*.

The next result of chemical action is, *the production of forms of matter possessed of properties entirely distinct from those of their component parts*, so that it is impossible to anticipate, from our knowledge of the characters of the latter, those which are to belong to the resulting compound: hence chemistry is essentially a science of *experiment*. Oil of vitriol, for instance, or *sulphuric acid*, is a highly acrid and corrosive liquid, but it is composed of tasteless and comparatively inert elements, namely, oxygen, sulphur, and water. The elements, oxygen and nitrogen, which, in a state of *mechanical mixture*, constitute the air we breathe, give rise, when *chemically combined*, to one of the most active agents of the laboratory; namely, *nitrous acid*. Again, if sulphuric or nitric acids be combined with caustic potassa, comparatively mild and inert *neutral salts* result, namely, the *sulphate* and the *nitrate of potassa*, in which none of the properties of the component acid and alkali can be recognised. In art, these remarkable changes are made subservient to the most important purposes. A variety of extremely useful compounds are obtained by the union of elements comparatively useless and unimportant; and, by the decomposition of apparently insignificant compounds, their more useful and important elements or components are separated. In nature, analogous changes are more strikingly presented to our observation, and the flower, the shrub, and the tree, are seen gradually to be formed and developed out of materials contributed by the air and soil, and in all respects most dissimilar to the new products of the vegetable: it is true that in these, and in analogous cases which might be taken from the animal kingdom, the mysterious power of vitality interposes; but such changes are nevertheless *chemical*, and legitimate objects of chemical inquiry.

There are many beautiful experiments illustrative of the total change of all obvious properties of substances as a consequence of chemical combination; as one striking instance, we may adduce the mutual action of *oxygen and nitrous gases*; these bodies are respectively permanently

elastic fluids, without color, taste, or smell: when mixed over water, they immediately enter into chemical combination, lose their elastic form, become of a deep orange color, intensely sour, and of a peculiar odor; in their separate state they are insoluble in water, but the body which has resulted from their combination is perfectly soluble in that fluid.

Change of color is a common, but also an important, result of chemical action. By exposure to light, air, and moisture, the greater number of colors are gradually destroyed, in consequence of the chemical agencies that ensue; a similar destruction of color takes place more immediately upon the application of chlorine; and hence these agents are resorted to, to effect the purpose of *bleaching*. In the arts of *dyeing* and *calico-printing*, not only are fugitive colors rendered permanent, but their tints are variously modified by chemical means. Of the vegetable blues, there are many which are rendered *red* by an acid, and *green* by an alkali; and hence paper stained by the juice of violets, or of the blue flag, or of the petals of the blue heart's-ease, is useful as a *test* of the presence of alkaline bodies. The same principle is applied to other purposes: if, for instance, an acid be gradually added to an alkaline solution, it is found that there are certain proportions in which they exactly *neutralize* each other; that is, a point at which the liquid neither exhibits acid nor alkaline characters. This point may be precisely learned by the above tests, for the solution then has no effect on the vegetable blue; but if either acid or alkali be predominant, that is, if the point of neutralization has not been exactly attained, then the test, by the tint which it assumes, announces the predominant element: *green*, if alkaline, and *red*, if acid*.

In other cases, change of *color* announces the presence of peculiar elements or compounds: thus ferrocyanide of potassium shows iron by a *blue* color, copper by a *brown*, nickel by a very *pale green*, &c., and there are numberless other tests applicable upon the same principle.

Among the results of chemical action, we may next notice those which relate to the *change of state or form, sustained by the acting bodies*. When substances are burned in the air, they generally pass, as already observed, from the *solid* to the *aëriform* state; and the deflagration of gunpowder is a good instance of such sudden conversion; the converse change, that of *gases* into *solids*, is not so common, yet such cases are not unfrequent. When, for instance, ammonia and hydrochloric acid, both *gaseous*, are mixed, they immediately condense into a white salt, which is *hydrochlorate of ammonia*. When one part of fuming nitric acid is added to two of strong alcohol, the *liquids* presently disappear, with violent ebullition, in the form of an inflammable *vapor*; and when

* The *test-papers* used in the laboratory are generally *blue litmus* paper, for the detection of acids, and the same *reddened by a weak acid*, for the detection of alkalis; the acids render the former *red*, and the alkalis restore the *blue* of the latter. Paper tinged yellow by *turmeric* is also useful in the detection of alkalis, which change it to a more or less deep *reddish brown*.

Unsize paper, tinged by a strong infusion of the petals of the red rose, is a more delicate test for alkalis than turmeric: in a very strong alkali it is turned greenish brown, but when the alkaline solution is very dilute, its reaction is extremely delicate, and it becomes bright green: it will thus indicate alkali where turmeric is not visibly discolored. (A. TAYLOR.)

chlorine and bicarburetted hydrogen *gases* are mixed, they form a *liquid* of the appearance of oil.

Liquids by combination produce *solids*, and *solids* produce *liquids*. A strong solution of chloride of calcium, mixed with one of carbonate of potassa, soon concrete when shaken together. Excess of a strong solution of tartaric acid, added to strong liquid ammonia, solidify into *bitartrate of ammonia*, with the evolution of *heat*. A mixture of pure alcohol added to a saturated solution of sulphate of magnesia, congeals into a crystallized solid. Crystals of sulphate of soda, rubbed with an equal quantity of nitrate of ammonia, gradually form a liquid. So also the solid amalgams of lead and bismuth, when triturated together, assume a liquid form, and become *cold*.

§ 2. THEORY OF COMBINATION AND DECOMPOSITION.

CHEMICAL affinity is frequently spoken of under the term *elective attraction*, and is said to be either *simple* or *complex*. It is sufficiently obvious that different bodies are possessed of different attractive powers: and accordingly, if several be brought together, those which have the strongest mutual attractions will enter first into union: hence has arisen the above term. If I pour dilute nitric acid upon a mixture of lime and magnesia, the acid will dissolve the lime in preference to the magnesia. The knowledge of this fact leads to the inference that lime would separate magnesia from its combination with nitric acid; and, accordingly, if lime-water be added to a solution of nitrate of magnesia, nitrate of lime is formed, and magnesia is thrown down or *precipitated*.

Upon this principle *tables of attraction* have been constructed, in which the substance, whose affinities are to be represented, is placed at the head of a column, and the bodies with which it combines beneath it, in the order of their respective attractions; thus the affinity of *sulphuric acid* for several bases would be shown as annexed.

SULPHURIC ACID.

—
Baryta.
Strontia.
Potassa.
Soda.
Lime.
Magnesia.
Ammonia.

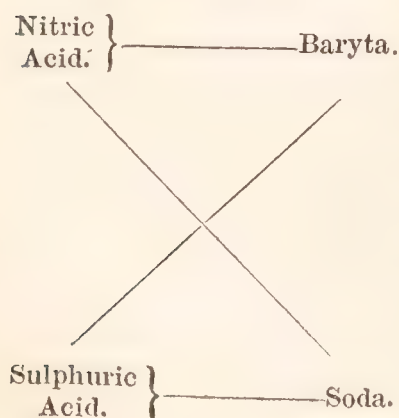
From this table it would appear that *baryta* separates sulphuric acid from its compounds with all the inferior substances, and that *ammonia* is separated by all that are above it. There are, however, many circumstances which interfere with the accuracy of such tables; in some cases the volatility, and in others the insolubility of one or other products, influence the results; and sometimes there are apparent anomalies in the mutual agencies of bodies, which subvert the order of arrangement. This is especially the case in the decomposition of certain insoluble compounds by soluble salts. One of these, originally noticed by Dulong, (*Ann. de Chim.*, LXXXII., NICHOLSON'S *Journ.*, Nos. 35 and 36,) has been investigated by R. Phillips (*Journal of Science and the Arts*, i. 80). He found that, on boiling carbonate of baryta in a solution of sulphate of potassa, sulphate of baryta and carbonate of potassa were formed; and he also found that, on reversing the experiment, by boiling sulphate of baryta in a solution of carbonate of potassa, carbonate of baryta and sulphate of potassa were produced. The inferences deducible from Dulong's researches upon this subject are, that all the insoluble salts are decomposed by the carbonates of potassa or soda; but that a mutual exchange of principles of these salts cannot in any case be complete: and

that all the soluble salts, of which the acid forms with the base of the insoluble carbonate an insoluble salt, are decomposed by these carbonates until the decomposition has reached a certain limit, which it does not pass. (URE'S *Dict.*, Art. ATTRACTION.)

In the mutual decompositions of steam by iron, and of oxide of iron by hydrogen, we have another apparently anomalous case of chemical action. When steam is passed over red-hot iron, a portion of it is decomposed, hydrogen gas is evolved, and oxide of iron is formed; whence we should infer that the affinity of oxygen is greater for iron than for hydrogen. But if hydrogen gas be passed over red-hot oxide of iron, steam is formed and the iron reduced to the metallic state; here the affinity of oxygen appears greater for hydrogen than for iron. In regard to this result it has been remarked by Professor Graham (*Elem. of Chem.*, Part 2), "that it is obviously connected with the relative proportion between the hydrogen and the steam which are at once in contact with the metal and its oxide at a red heat. When steam is in excess, water is decomposed, but when hydrogen is in excess, oxide of iron is decomposed; and why? because the excess of steam in the first case is an atmosphere into which hydrogen can diffuse, and the disengagement of that gas is therefore procured; but in the second case the atmosphere is principally hydrogen, and represses the evolution of more hydrogen but facilitates that of steam. The affinity of iron and hydrogen for oxygen, at the temperature of the experiments, is so nearly balanced, that the one affinity prevails over the other, according as there is a proper atmosphere into which the gaseous product of its action may diffuse. This affords an intelligible instance of the influence of mass or quantity of material, in promoting a chemical change; the steam, or the hydrogen, as it preponderates, exerting a specific influence in the capacity of a gaseous atmosphere." The subject of the diffusion of gases referred to in this quotation will be explained in the chapter on *Hydrogen*.

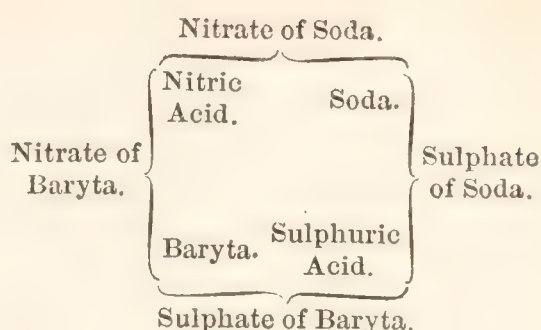
In cases of *simple attraction*, or affinity, one body separates another from its combination with a third. Thus, when potassa is added to a solution of sulphate of zinc (composed of sulphuric acid and oxide of zinc), the oxide of zinc is separated, and sulphate of potassa is produced; or when sulphuric acid is dropped into a solution of nitrate of baryta, sulphate of baryta is precipitated and nitric acid set free.

In cases of *double decomposition*, two new compounds are produced: as when a solution of nitrate of baryta is mixed with a solution of sulphate of soda, the results are a precipitate of sulphate of baryta, and a solution of nitrate of soda.



These cases of double decomposition are sometimes conveniently illustrated by *diagrams*; which may either be constructed so as merely to show the result of the change, or, where required, they may also exhibit the composition of the acting bodies. In the case just alluded to, the substances before mixture are shown by parallel lines, and after mixture by diagonal lines.

Or a more complete view of the change is given in the annexed diagram, where the bodies, before mixture, are placed upon the outside of the perpendicular lines: their component parts are shown within them; and the new results on the outside of the horizontal lines.



§ 3. CHEMICAL EQUIVALENTS AND THE ATOMIC THEORY.

A MOST important result of chemical attraction is, *that bodies combine in certain proportions only*. Thus, in the case just cited, of the combination of baryta with sulphuric acid, to form *sulphate of baryta*, it is found, that in that compound, whether formed by nature or art, by single or double decomposition, the sulphuric acid and baryta always bear a certain definite relation to each other, and are contained in it in the relative proportions, by weight, of 40 sulphuric acid and 77 baryta: that is, these relative weights exactly saturate or neutralize each other; if we suppose sulphate of baryta to be composed of *one atom* of sulphuric acid and *one atom* of baryta, then the above numbers may be called the *atomic weights* of those substances, and an atom of sulphuric acid being = 40 and of baryta = 77, the atom of sulphate of baryta will be $(40 + 77) = 117$: these numerical proportions have been sometimes called *representative, or combining numbers*; or more commonly, for a reason which will presently be apparent, *equivalent numbers* or *proportionals*.

But, sulphuric acid and baryta are not elementary substances, they are both compounds, and are consequently termed the *proximate elements* of sulphate of baryta; sulphuric acid consists of sulphur and oxygen, and baryta consists of barium and oxygen; the *ultimate elements*, therefore, of sulphate of baryta, are sulphur, barium, and oxygen: hence also sulphuric acid and baryta are called *compound atoms*; but, in them, the same general law of definite proportionals holds good, for sulphuric acid consists of 16 sulphur and 24 oxygen, which, added together, produce the *compound equivalent* 40; and baryta consists of 69 barium and 8 oxygen, making 77, the *equivalent* of baryta or oxide of barium.

Another essential fact in reference to chemical combination is, that where one substance, A, combines in more than one proportion with another substance, B, the second, third, &c., proportions of B bear a very simple ratio to each other. Thus, mercury combines with oxygen in two proportions, forming the *black oxide* and the *red oxide* of mercury. In the former, 200 parts of mercury are combined with 8 of oxygen, and in the latter, 200 parts of mercury are combined with 16 of oxygen. Here it is obvious that the quantity of oxygen in the *first*, is to that in the *second* compound as 1 to 2. So that, assuming 200 to be the atomic weight of mercury, and 8 the atomic weight of oxygen, we should call the *black oxide* a compound of 1 *atom* of mercury and 1 *atom* of oxygen, and the *red oxide* a compound of 1 *atom* of mercury and 2 *atoms* of oxygen.

In other cases, the relative proportions of the components are to each other, as 1 to $1\frac{1}{2}$, 1 to $2\frac{1}{2}$, &c.; or, what amounts to the same thing, as 2 to 3, 2 to 5, &c. Thus, in regard to two of the oxides of iron: in the *protoxide*, 28 parts of iron are combined with 8 of oxygen, and in the

peroxide with 12 of oxygen. Here, the quantity of oxygen in the *first* is to that in the *second* as 1 to 1·5. There are also two acids of arsenic; in the *arsenious acid*, 75 parts of arsenic are combined with 24 of oxygen, and in the *arsenic acid* with 40 of oxygen; numbers which are to each other as 3 to 5. These cases, however, are by no means of such frequent occurrence as the former.

The simple ratio which the *weights* of the combining elements are thus seen to bear to each other, involves an equally simple law in respect to combining *volumes*, where substances either exist, or may be supposed to exist, in the state of gas or vapour. Thus, water may be considered as a compound of one atom of hydrogen and 1 atom of oxygen, the relative weights of which are to each other as 1 to 8; hence the equivalent of the atom of water will be (1 hydrogen + 8 oxygen) = 9. But oxygen and hydrogen exist in the gaseous state, and the weights of equal *volumes* of those gases (or in other words, their relative densities, or specific gravities), are to each other as 1 to 16; hence 1 *volume* of hydrogen is combined with $\frac{1}{2}$ a *volume* of oxygen, to form 1 *volume* of the vapor of water

Hydrogen. 1	Oxygen. 8	=	Steam. 9
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or steam: for the specific gravity of steam, compared with hydrogen, is as 9 to 1. The annexed diagrams, therefore, will represent the combining *weights* and *volumes* of the elements of water, and of its vapor.

To give another instance: hydrochloric acid gas is considered as a compound of 1 atom of hydrogen and 1 atom of chlorine, their respective *weights* being 1 and 36, and that of the resulting hydrochloric acid 37. Now the specific gravity of hydrogen to chlorine is also as 1 to 36, and

Hydrogen. 1	Chlorine. 36	=	Hydrochloric Acid. 37
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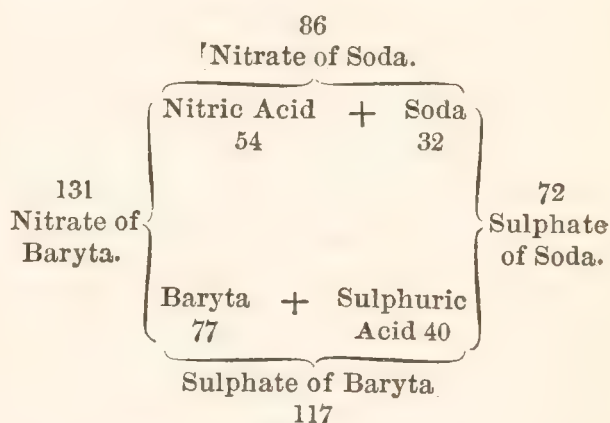
of hydrogen to hydrochloric acid as 1 to 18·5. Hence it is obvious, as in this diagram, that 1 *volume* of hydrogen and 1 *volume* of chlorine combine to form 2 *volumes* of hydrochloric acid.

These instances, therefore, will suffice to show that there is the same simple relation in the *volumes* of the compounds as in their *weights*; 1 volume of hydrogen and 0·5 a volume of oxygen producing 1 volume of aqueous vapour; and 1 volume of hydrogen and 1 volume of chlorine producing 2 volumes of hydrochloric acid. In the latter case, and there are many similar instances, the equivalent, or atomic *weights*, correspond with the specific gravities in reference to hydrogen as = 1, the gases combining volume for volume, and producing a compound gas, the volume of which is equal to the united volumes of its constituents.

As a further illustration of the whole subject of definite proportionals, and of the atomic theory, in reference to weights and volumes, I subjoin a table of the compounds of *nitrogen* and *oxygen*: those elementary bodies unite with each other in no less than 5 proportions, and in the simplest ratios, forming two oxides and three acids.

	Atoms or equivalents of Nitrogen and Oxygen.		Weights of the atoms or equivalents of Nitrogen and Oxygen.		Atomic weight of the compound.	Volumes of Nitrogen and Oxygen.		Resulting volume of the compound.
	N.	O.	N.	O.		N.	O.	
1 atom of the protoxide of } nitrogen consists of....}	1	1	14	8	22	1	0.5	1
1 atom of the deutoxide	1	2	14	16	30	1	1	2
1 atom of the hyponitrous } acid	1	3	14	24	38	1	1.5	...
1 atom of the nitrous acid....	1	4	14	32	46	1	2	1
1 atom of the nitric acid	1	5	14	40	54	1	2.5	...

It has been above stated that 40 parts of sulphuric acid (or 1 atom) are neutralized by 77 (or 1 atom) of *baryta*. Now we find that 40 parts of sulphuric acid are neutralized by 32 of *soda*; hence, 32 will be the atomic weight, or equivalent of *soda*: if we now refer to nitric acid we shall find that 77 parts of *baryta* neutralize 54 of nitric acid, and that 32 of *soda* neutralize the same quantity of that acid. Supposing, therefore, we decompose *nitrate of baryta* by *sulphate of soda*, it follows that the newly-formed salts will still be *neutral*, as in the subjoined diagram, to which the *equivalent* numbers of the acting substances are annexed; from which it appears that 131 parts of *nitrate of baryta*, consisting of 77 *baryta* and 54 nitric acid, are required to decompose 72 parts of *sulphate of soda*, composed of 32 *soda* and 40 sulphuric acid; and that the results of this decomposition are 86 parts of *nitrate of soda*, composed of 54 nitric acid and 32 *soda*, and 117 *sulphate of baryta*, composed of 40 sulphuric acid and 77 *baryta*.



If we, therefore, are acquainted with the *equivalent numbers* of the respective *bases* and *acids*, we at once know the relative quantities required for *saturation*, and consequently the composition of all the *neutral salts*, as will be evident from inspecting the following table:—

ACID.	EQUIVALENT.	BASE.	EQUIVALENT.
Iodic	165	Baryta	77
Bromic	118	Strontia	52
Chloric	76	Potassa	48
Selenic	64	Soda	32
Nitric	54	Lime	28
Sulphuric	40	Magnesia	20
Oxalic	36	Ammonia	17
Carbonic	22	Lithia	15

Here we find, for instance, that 40 parts of sulphuric acid saturate 48 of potassa to form 88 of *sulphate of potassa*, for the decomposition of which would be required 131 of *nitrate of baryta*, containing 54 of nitric acid and 77 of *baryta*. We may also remark the different quantities of the different bases that are required to saturate a given weight of any of the acids, and *vice versâ*: thus, 77 of *baryta*, and only 17 of ammonia, are required to saturate 54 of nitric acid; and 28 of lime, which are saturated by 22 of carbonic acid, require 165 of iodic acid for the same purpose.

These tables are of great value to those who conduct chemical operations upon the large scale, in the processes of arts and manufactures, guiding them in the quantity of materials which they require, and pointing out the proportions of the products which should be obtained; and when applied, as suggested by Dr. Wollaston in his account of “A Synoptic Scale of Chemical Equivalents,” (*Phil. Trans.*, 1814,) to a *sliding-rule*, divided upon the principles of *Gunter’s scale*, they furnish the practical as well as the theoretical chemist with an admirable instrument of reference, for the purpose of facilitating and verifying his experimental and calculated results. The form of this instrument, which I recommend to the student*, is a box-wood scale, about two feet two inches long, consisting of a moveable slider with a logometric line of numbers upon it, and a corresponding series of numbers upon the rule itself; upon the *rule* the simple substances are also arranged, each opposite to its respective equivalent: the equivalents of the compounds may, by those who have competent experience, be easily deduced from those of the elements; but, for the convenience of others, and to avoid perplexing the scale with a multiplicity of terms, a separate table accompanies it, containing a copious list of compound equivalents. One of the commonest uses of this scale is to ascertain the relative proportions of the elements, in variable quantities of their compounds; for instance, I know that the equivalent of *chlorine* is 36, and of *sodium* 24, and consequently that the equivalent of *chloride of sodium* (or common salt) is $(36 + 24) = 60$. But I wish to ascertain how much of each of the elements is contained in 95 of salt: I therefore bring the number 95 upon the slider opposite to 60 upon the scale, and I now find the number 57 opposite to 36, and the number 38 opposite to 24; hence 95 parts of *chloride of sodium* consist of 57 of *chlorine*, and 38 *sodium*. These and the other uses of this scale are soon learned by a little practice, or by reference to Dr. Wollaston’s paper, above quoted, or to FARADAY’S *Manipulation*.

The doctrine of equivalents furnishes the analytical chemist, in the first place, with a valuable test of the accuracy of his experimental results, which of course, if correct, will not deviate from the above laws; it also enables him, in many instances, to infer the composition of a substance, where direct experiment is unattainable, and this in more ways than one. It was long, for instance, before *magnesium* (the metallic base of magnesia,) was obtained, but analogy led chemists to conclude that magnesia was a *protoxide* of a metal, that is, a compound of 1 atom of metallic base, with 1 atom of oxygen. The composition of magnesia, therefore, was inferred from the composition of its *sulphate*, consisting of 1 atom of sulphuric acid $= 40$ united to 20 of magnesia; now 20, which thus presents itself as the atomic weight of magnesia, must include an atom of oxygen $= 8$; and 8 deducted from 20, leaves 12 as the inferred weight of the atom of *magnesium*. In the same way the composition of lime was inferred to be 20 calcium and 8 oxygen, for it was found that sulphate of lime consisted of 40 sulphuric acid and 28 lime, and as the oxygen in the *base* of a neutral

* They are made by Newman, No. 122, Regent-street, and tables of weights and measures, and of the different thermometric scales, may be conveniently added upon the back of the rule.

sulphate is to that in the *acid* as 1 to 3, it became obvious that *lime*, or *protoxide of calcium*, must be constituted as above stated.

To give another instance of a similar application of the atomic theory: it was found that chlorine expelled oxygen from lime, and it was ascertained that for every 28 parts of lime so decomposed, 8 parts of oxygen were evolved, and 56 parts of chloride of calcium formed; now deducting 36 (the equivalent of chlorine) from 56, 20 remains as the equivalent of calcium.

More complicated instances of such extensions of this theory will be given afterwards, especially among its applications to *organic products*; my object in the preceding paragraphs has been to divest it of all hypothetical difficulty, and to present it to the student as involving a series of important practical applications, and as founded upon the basis of experiment. Those who would view it in reference to ancient atomic doctrines, and to the more obscure parts of molecular philosophy, may consult Dr. DAUBENY'S *Essay on the Atomic Theory*, and Dr. PROUT'S *Bridgewater Treatise*.

I shall now merely add a few words in further explanation of the *mode of determining atomic weights, or equivalent numbers*. They are founded upon careful analyses of the simplest combinations of the most important elements: among these we may, as an instance, select *water*; the most rigid analytical researches concur in representing this fluid as constituted, *per cent.*, of 11.1 hydrogen, and 88.9 oxygen. Now, if we determine upon hydrogen as *unity*, or $= 1$, then $11.1 : 88.9 :: 1 : 8.009$; or, the hydrogen is to the oxygen very nearly in the ratio of 1 to 8; and assuming water to consist of 1 *atom* of hydrogen united to 1 *atom* of oxygen, the atomic weight of the former being $= 1$, that of the latter would be $= 8$. In *hydrochloric acid*, which, as already stated, is a compound of hydrogen and chlorine, these elements bear to each other the relation of 1 to 36; hence 36 is assumed as the *atomic weight*, or *prime equivalent* of chlorine. If I now wish to determine the equivalent of a *metal*, I select its *protoxide*, and ascertain what *weight* of the metal is combined in such oxide, with 8 parts of oxygen. Thus in regard to *soda*, I find it constituted *per cent.* of 25 oxygen and 75 sodium; and $25 : 75 :: 8 : 24$, hence the number 24 is assumed as the *equivalent of sodium*. In the same way I may resort to the analysis of *chloride of sodium*, 100 parts of which consist of 60 chlorine and 40 sodium; and $60 : 40 :: 36 : 24$; thus the former result is verified by the analysis of a second compound.

The advantages of assuming *hydrogen* as $= 1$ or *unity*, and thence deducing the other equivalents, are such as to have led to its very general adoption in this country; as it is the substance which combines in the smallest relative weight, all other substances may be represented by numbers which are *multiples* of its equivalent, and may, for all ordinary purposes of demonstration and research, be *whole numbers*; but to this subject I shall again recur. Some represent hydrogen by 10, and some by 100; in these cases oxygen is of course 80 or 800, and chlorine 360 or 3600, &c. Others adopt *oxygen* as *unity*, in which case hydrogen becomes one-eighth of that unit, and is represented by 0.125, chlorine by 4.5, sodium by 3, &c.; but this system is extremely inconvenient, in consequence of the perpetual and necessary recurrence of fractions,

especially as concerns the retention of equivalents by the memory. The equivalents used by Berzelius have reference to oxygen as 100*; and consequently his equivalent for hydrogen is 12·5, for $8 : 1 :: 100 : 12\cdot5$ or $8 : 1 :: 1\cdot00 : 0\cdot125$. To convert the equivalent on the hydrogen scale to that of the oxygen unit, divide the former by 8. Thus 36, which is the equivalent of chlorine on the hydrogen scale, gives 4·5 as its equivalent on the oxygen scale; or 450, if hydrogen be assumed as = to 100. To convert the oxygen equivalent into that of the hydrogen scale, multiply the former by 8; thus 4·5 gives 36, and 0·125, which is the equivalent of the hydrogen on the oxygen scale, multiplied by 8, gives 1. I have, in this work, used the terms *atom* and *equivalent* as synonymous, and they are generally so employed in this country. "On the Continent this has not been the case, for the *equivalent* of many elements, such as hydrogen, chlorine, &c., has there been assumed to contain *two atoms*." "But as both parties agree that water contains *one equivalent* of each element, it is obvious that the system adopted in Britain, by which equivalent is made entirely synonymous with atom, has the very great advantage of superior simplicity." "Within the last year or two several of the most distinguished chemists on the Continent have adopted the British system in this respect, and there is little doubt that ere long it will become universally prevalent." (GREGORY, *Outlines of Chemistry*, 25.)

The practical uses and applications of the atomic theory, and further illustrations of the researches upon which it is founded, will occur in almost every succeeding page of this book. It has been justly observed by Sir John Herschel, that the extreme simplicity which characterizes this theory, is itself no unequivocal indication of its elevated rank in the scale of physical truths.

* The extreme confusion resulting from the adoption of a series of equivalent numbers founded upon the assumption that water is a compound of 2 atoms of hydrogen and 1 atom of oxygen, and the incongruities and contradictions which that hypothesis involves, must be too evident to all who read the works of the eminent authors who speak in that language. We shall have other opportunities of adverting to the views of Dr. Prout in reference to the equivalents of the undecomposed substances being simple multiples of the hydrogen unit; a view which, though opposed and even ridiculed, has been elaborately examined into and verified by Dumas as regards the most important elements, namely, oxygen, nitrogen, carbon, calcium, &c. Upon the principle stated in the text, that for all ordinary purposes of research the equivalents may be represented by whole numbers; and under the conviction that analytic operations have not attained that consummate perfection which some have assumed, and which must be arrived at before this question can be settled, I have always employed Dr. Prout's num-

bers," and it is very satisfactory to find many of the highest authorities coming in to these views. Thus, Dumas observes: "J'ai dit, et je répète, que tous les poids atomiques ont besoin d'une révision attentive: que sans adopter ou sans repousser les opinions du Docteur Prout, je suis forcé de convenir qu'elles se sont généralement accordées à mes propres expériences." (*Ann. Ch. et Ph.*, Juin, 1843, p. 203.) Gmelin, too, has given his opinion in favour of the hydrogen unit, and has adopted it in his *Handbook*: and though he has not followed up the system of whole numbers throughout, he has adopted it in reference to oxygen, nitrogen, carbon, sulphur, &c. And in regard to *chlorine*, which many experienced analysts have held out as insurmountably incompatible with Prout's doctrine of whole numbers, it has been shown by Gerhardt, (*Comptes Rendus*, &c., Dec. 8, 1845,) that in adopting certain manipulatory precautions which his predecessors had neglected, he arrives exactly at the simple multiple 36, for its equivalent upon the hydrogen scale.

CHAPTER IV.

ELECTRICITY.

MANY of the phenomena of electricity are so remarkable, and so easily exhibited, as long to have attracted general attention: by the natural philosopher they have been studied with much precision and success; and, more lately the discovery of the relation of the *electrical* to the *chemical* powers of matter, and to *magnetism*, has opened an entirely new field of research.

We are ignorant of the *nature* or *cause* of electrical phenomena, but for the convenience of description and discussion it has been customary to refer them to the presence of a highly attenuated and subtile form of matter, which has been termed the *electric fluid*. The existence, however, of such a fluid, or of any peculiar form of matter as productive of electrical phenomena, is entirely hypothetical, and merely assumed to facilitate our reasoning upon the subject.

Inasmuch as electrified bodies are found to present themselves in *two opposite or distinct states*, it has been presumed that the electric fluid exists in all forms of matter; that, under ordinary circumstances, it is in *a state of equilibrium or quiescence*; and that, when this state is so disturbed as to occasion either its *redundance* or *deficiency*, the bodies then become *electrically excited*: upon this view of the cause of electricity, which originated with Franklin, the opposite states have been termed *positive* and *negative*. Others ascribe the phenomena to the presence of *two electric fluids*, supposed to reside in *glass* and *resin*, and hence distinguished by the terms *vitreous* and *resinous*. This hypothesis, which originated with Du Fay, has, under some modifications, also been very generally adopted; it has been assumed that the two electric fluids are universally diffused; that they are infinitely subtile and elastic, and each *repulsive of its own particles, but attractive of those of the opposite kind*; these forces being equal at equal distances, and varying inversely with the square of the distance*. In the ordinary or quiescent state, these fluids are supposed to be *combined* with, and exactly to *neutralize*, each other; and electric excitation is attributed to their *separation*, or to the *decomposition* of the neutral fluid. The first of these hypotheses is recommended by its simplicity, and by the facility with which it enables us to reason upon the greater number of electrical phenomena; but there are cases in which the second appears most consistent; so long, however, as the definitions which we shall afterwards give, of the terms *positive* and *negative*, are distinctly understood, the adoption of either hypothesis is matter of little importance, always bearing in mind that both states, or fluids, are common to all matter, and that they are always co-existent.

§ 1. ELECTRICAL EXCITATION. ATTRACTION AND REPULSION.

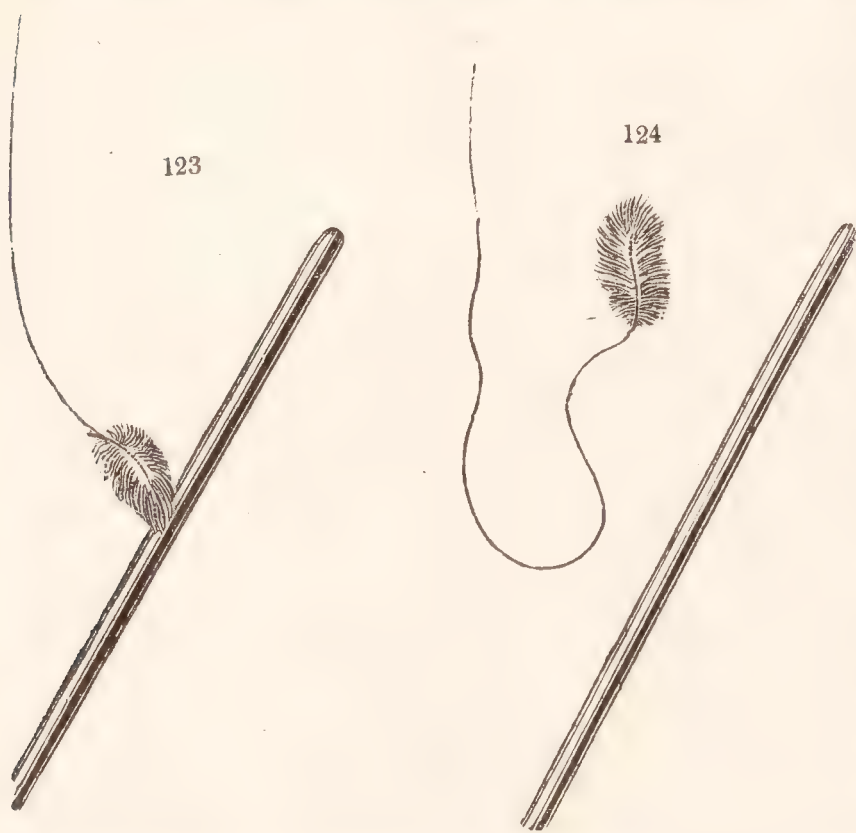
THE simplest indication of electricity is that observed when certain resinous and vitreous bodies are subjected, in a dry and warm state, to

* Coulomb supposed the two electric fluids to be possessed of equivalent properties, neutralizing each other's elasticity like oxygen and hydrogen combined.

gentle friction; as when a piece of sealing-wax is rubbed with flannel, or a glass rod with a piece of silk; in these cases the sealing-wax and the glass acquire the property of attracting and repelling light substances; and they are said to be *electrically excited*. Such properties seem first to have been observed in, and supposed peculiar to *amber*; and hence the term *electricity*, from the Greek word *ηλεκτρον*, signifying *amber*. Independent of these attractive and repulsive powers, there are other equally curious properties observed in the electrically-excited bodies; in the dark they appear *luminous*, emitting, whilst rubbed, flashes of bluish light; and, if held near the face, they produce a singular tickling sensation. We find, moreover, that this electrical excitation is transient; that it gradually disappears, and that if the hand be passed two or three times over the surface of the sealing-wax, or of the glass, all signs of electricity are lost. A light downy feather, clean and dry, and suspended by a long thread of *white* sewing silk, so as to be as independent as possible of surrounding bodies, is a most delicate and useful indicator of this form of electrical excitation, and may be used in the following experiments.

1. Provide a glass tube, about three feet long, and three-fourths of an inch diameter, and having wiped it perfectly clean and dry, rub it gently with a warm silk handkerchief; it will become electrically excited; and, on approaching the feather, will immediately *attract* it; but, on gently withdrawing, and again bringing it near to the feather, the feather will

be steadily *repelled*; so that it will be impossible, for a short time, to get it to touch the tube: after a while, however, it again flies to, or is attracted by, the tube, and then again repelled as before. The annexed cuts (figs. 123, 124,) represent the appearance of the feather when attracted and when repelled.



This apparently trifling experiment teaches an important elementary fact: it shows that the feather, having received electricity from the glass by direct contact, is repelled by it; and, consequently, that *bodies similarly electrified repel each other*; for we assume the feather to have received a portion of the electricity of the glass, and we know that the repulsion is *mutual*.

2. Rub a large stick of red sealing-wax with a piece of dry and warm flannel; the sealing-wax will thus be rendered electrical, and will act upon the feather *apparently* in the same way as the glass; that is, first attracting and then repelling it; and the moment that the feather has received the electricity of the wax, those bodies also become mutually repulsive.

3. Warm a sheet of foolscap paper, folded in the usual way, before the fire, and rub it gently upon a clean polished table with a piece of Indian rubber; then suddenly open the sheet, and hold its interior towards the feather, which will be attracted and repelled, as in the preceding cases of glass and wax.

There are a number of other substances which become electrical by friction, such as white and black silk drawn gently over each other, as is commonly observed with silk stockings; the back of a clean cat gently rubbed with the dry and warm hand; long, clean, and dry hair, combed in frosty weather; silk tassels and fringes, and so on: but the instances above cited are sufficient, and we may now proceed to a second set of experiments with the same apparatus.

1. Excite the glass tube as before, and electrize the feather, so as to render it *repulsive* of the tube; then bring the excited sealing-wax near the feather, and it will not be repelled as by the glass, but will be immediately *attracted*, by it.

2. Reverse the experiment, and having electrized the feather by sealing-wax, bring the excited glass rod near it, when, instead of being further *repelled*, it will be *attracted*.

3. If the feather be suspended between the excited wax and the excited glass, it will vibrate to and fro, being *alternately attracted and repelled*.

These experiments show that there is a *difference in the electricities of the glass and sealing-wax*, and that bodies rendered *repulsive* by glass are *attracted* by wax; and *vice versâ*. We had previously found that bodies similarly electrified repel each other; we now observe that *bodies dissimilarly electrified attract each other*.

These dissimilar electricities, in reference especially to the above methods of producing them, were originally termed *vitreous* and *resinous*; for these, the terms *positive* and *negative* are now more commonly substituted; and the two states may be represented by the symbols *plus*, + and *minus*, -. The feather electrified by *glass* is said to be in a *positive* state, and that by *sealing-wax*, *negative*.

Still retaining the simple apparatus that we set out with, we may now proceed as follows: 1. Fold the silk in such a way as to keep the hand as far as possible from the glass tube; then rub the tube with it, and electrize the feather, which will now be *repelled*; whilst it retains this repulsive state in regard to the tube, approach it with the part of the silk which had rubbed the glass, and it will be found to be *attracted*. From this experiment we should conclude that the *silk* and the *glass* were in *opposite* electric states: we have already called the glass *positive*; the silk, therefore, must be *negative*. The experiment may be varied as follows:

2. Hold the silk as before, and having warmed it, rub it with the tube; then bring it near the feather, which it will at first attract and then repel: whilst the feather is thus *repelled* by the silk, approach it with the excited glass, by which it will be immediately *attracted*. It is obvious, therefore, that the glass and the silk are in *opposite* states.

3. If we roll up the flannel so as to keep the rubbed part at a distance from the hand, then rub it with the sealing-wax, and bring it to the

feather, the latter will be immediately attracted by the flannel, and then repelled: if we now approach it with the excited wax, instead of being more powerfully *repelled*, it will be instantly *attracted*. Hence, having agreed to call the electricity of the wax *negative*, that of the flannel must of course be *positive*; for it is evidently of the opposite or dissimilar kind.

Here, then, we have developed another important electrical law, showing that *one kind of electricity cannot be produced without the other*; that when a body is *positive*, some part of the exciting arrangement is *negative*. In the above case of glass and silk, the former is positive, and the latter negative: and in the case of sealing-wax rubbed by flannel, the wax is negative, and the rubber acquires a positive state.

4. That this is so, may be further shown as follows: render the feather positive by the contact of the excited glass; then approach it with the excited flannel, and it will be found to be repulsive of the flannel; that is, to possess a *similar* electrical state.

5. Electrize the feather with the excited wax, which will render it *negative*, and then approach it with the excited silk; the silk will continue to repel the feather, and hence is similarly electrized, or *negative*.

Delicate instruments show us, that in almost all cases of *friction*, under the precautions above described, bodies become electrically excited: and that the same body may become either positive or negative, according to the circumstances under which it is excited. Smooth glass, for instance, becomes positive when rubbed with a piece of woollen cloth, but rough glass rubbed in the same way becomes negative; and sealing-wax, which becomes negative when rubbed by flannel, becomes positive when rubbed against tin-foil or mercury. A cat's back is said always to exhibit positive electricity; but it is probable that no peculiar kind of electricity is inherent in any one body: it will even vary with the mechanical state of the surface and the mode of friction; so polished glass becomes positive when rubbed upon silk, but rough glass becomes negative; both become negative against a cat's back; and when similar substances are rubbed together, that, the friction of which is limited to the least extent of surface, is usually negative: thus, when two similar silk ribands are excited by drawing the one lengthways over the other, that which has suffered friction on its own length becomes positive, and the other negative. The following table, chiefly from the experiments of Cavallo, further illustrates these effects. (SINGER'S *Elements of Electricity*, p. 33.)

	<i>Becomes</i>	<i>by friction with</i>
The back of a cat	Positive	Every substance tried.
Smooth glass	Positive	Everything except cat-skin.
Rough glass	Positive	Dry oiled silk, sulphur metals.
	Negative.....	Wools, quills, wood, paper, sealing-wax, white-wax, common silk; the hand.
Tourmaline	Positive	Amber; air from bellows.
	Negative.....	Diamonds; the hand.
Hare's-skin	Positive	Metals, silk, leather, hand, paper, baked wood.
	Negative.....	Other finer furs.

	<i>Becomes</i>	<i>by friction with</i>
White silk.....	Positive	Black silk, metals, black cloth.
	Negative.....	Paper, hand, hair, weasel's skin.
Black silk	Positive	Sealing-wax.
	Negative.....	Hare, weasel, and ferret fur; brass, silver, iron, hand, white silk.
Sealing-wax	Positive	Some metals.
	Negative.....	Hare, weasel, and ferret fur, hand, leather, woollen cloth, paper, some metals.
Baked wood	Positive	Silk.
	Negative.....	Flannel.

In regard to the above table, Singer observes that iron, lead, and bismuth, render sealing-wax negative, the other metals positive; but the least difference in the condition of the materials occasions varieties in the result: with the same rubber (an iron chain) positive electricity may be excited in one stick of wax, and negative in another, if the former be scratched and the latter smooth. Æpinus also found that two pieces of plate-glass, when rubbed on each other, were electrical when separated; but that although one was always positive and the other negative, the same plate sometimes exhibited the one, and sometimes the other electricity.

In the following list, the substances become positive with those which follow, but negative with those which precede each other; viz., oxalate of lime, fur, smooth glass, woollen cloth, feathers, paper, silk, gum-lac, rough glass.

§ 2. ELECTRICAL CONDUCTORS AND NON-CONDUCTORS.

THERE are some substances which, when examined by the above-described methods, are not observed to become electrical. If we, for instance, rub a cylinder of *metal* with flannel or silk, it is perfectly inert when brought near the feather: but the exception here is apparent only; the substances previously used, such as glass and sealing-wax, are *non-conductors* of electricity; that is, they receive and retain it upon the excited surface only; but a bar of metal is a *conductor*, and when electricity is produced upon it by friction, it immediately spreads over its whole surface, and is carried off, as it were, by the hand, to the earth and all surrounding conductors. To show that the metal is actually excited in the same way as glass, attach it to some non-conductor: for instance, attach a cylinder or plate of brass to a stick of sealing-wax, which may serve as its handle; then rub the brass against a dry and warm flannel, and, taking care not to touch any part of it with the hand, bring it near the feather, which will be attracted, and then repelled, precisely as by the glass and wax. In these cases the metals usually acquire negative electricity.

We now, then, can understand the division of bodies into *conductors* and *non-conductors*. There are also a set of bodies intermediate between the above extremes, which are called *imperfect conductors*. The non-conductors, readily exhibiting their electricity by friction, are often called *electrics*, in opposition to the metals and other good conductors, which are called *non-electrics*. The electrics, from their power of preventing the passage or transfer and escape of electricity, are also sometimes

termed *insulators*. Thus, a brass rod mounted upon a stem or foot of glass or sealing-wax, or a wire suspended by silk thread, is said to be an *insulated conductor*. The insulators have also, in reference to other properties which they possess, and which will presently be adverted to, been termed *dielectrics*.

The metals are by far the most perfect conductors; next to them come well-burned charcoal and plumbago; then some of the concentrated acids, and strong saline solutions. Water, rarefied air, vapors, and many stony bodies and metallic ores, are imperfect conductors. Shell-lac is one of the most perfect non-conductors, and an excellent substance to use wherever good insulation is required*. Sulphur and wax are also non-conductors; and so is glass, which, though in this respect much inferior to some other substances, is, from the convenience of its application, the usual insulator employed in all common electrical apparatus. Raw and bleached silk stands high upon the list of non-conducting substances; but dyed silk is often a partial conductor, in consequence of the substances used to color it: hence, in the above experiments, we have advised *white* silk for the suspension and insulation of the feather. It is also stated by Henley, that black hair conducts better than white (*Phil. Trans.*, 1776), as illustrated in the case of a bullock struck by lightning. Dry air, and baked wood, are non-conductors. There is a gradual transition in bodies from what are termed perfect conductors, to perfect non-conductors; the following list exhibits the principal of these:—

CONDUCTORS.	IMPERFECT CONDUCTORS.	NON-CONDUCTORS.
Metals	Water	Spermaceti
Charcoal	Damp wood	Glass
Plumbago	Alcohol	Sulphur
Fused chlorides	Damp air	Fixed oils
—— iodides	Some oils	Resins
—— salts	Vegetable and	Ice
Strong acids	animal bodies	Diamond
—— alkaline solutions.	generally.	Shell-lac
		Oxalate of lime
		Dry gases and air.

There is no constant relation between the *states* of bodies and their conducting powers. Among *solids*, for instance, metals are conductors; resins non-conductors; among *liquids*, strong alkaline and acid solutions are good conductors; water is a very imperfect conductor; many oils are non-conductors. Potassa, protoxide of lead, chloride of sodium, iodide of zinc, many salts, and other bodies, are non-conductors in their solid state, but conduct when liquified by heat. Sulphur, phosphorus, resins, iodide of sulphur, and several other solid bodies, do not, on the contrary, acquire conducting power on assuming the liquid state. (FARADAY, *Experimental Researches*, § 394, &c.) Glass, when cold, is a non-conductor; but when red-hot, it is a conductor: carbon, in the form of the diamond

* According to Erman (*GILB. Ann.*, xi., 143), a thread of gum-lac insulates ten times as well as silk. A needle of sealing-wax remains for some days excited. A capillary bore lessens the insulating power of glass. The dissipation of electricity by

the atmosphere is nearly in the triplicate ratio of its moisture. It is also stated, that an electric jar is discharged if put into a vibratory state, as by sounding it like a harmonica.

is a non-conductor : but pure and well-burned charcoal, which is merely another form of carbon, is among the best non-metallic conductors*.

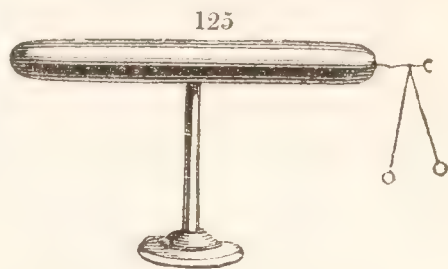
We may form some idea of the retardation which electricity suffers in passing through imperfect conductors, from the statement of Mr. Cavendish (*Phil. Trans.*, 1776), according to whom, iron-wire conducts 400 million times better than pure water ; sea-water (with one-thirtieth of salt), 100 times better ; and a saturated solution of salt, 700 times better.

The enormous rapidity of the progress, or supposed progress of the electric fluid through long trains of conductors, was first experimented upon by Watson (*Phil. Trans.*, 1748): he could observe no perceptible time occupied in its passage through a circuit of 12,276 feet. This curious subject has also been investigated by Wheatstone (*Phil. Trans.*, 1834, p. 583), according to whom, electricity moves through a copper wire, with the velocity of 400 feet in the ten-thousandth part of a second; or, through 4 million feet in a second. This is a velocity exceeding even that of light through space: he also found that the shock of a Leyden jar is transmitted from each end of an interposed wire, and arrives latest at the centre. To this subject we shall afterwards recur in referring to the conducting powers of the metals, in regard to voltaic electricity.

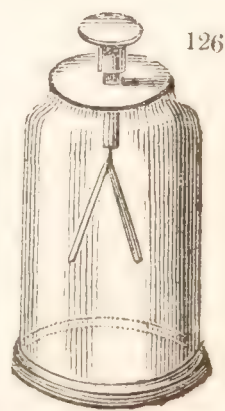
§ 3. ELECTROSCOPES AND ELECTROMETERS.

Electroscopes and *electrometers* are instruments by which changes in the electrical states of bodies are rendered evident, and their intensities measured.

One of the simplest of these (fig. 125) consists of two small pith-balls, suspended by very fine thread or silver-wire to the end of a small and well-insulated conductor: when this receives electricity, the balls diverge, and the nature of the electricity by which they are diverged may be judged of, by approaching the conductor with a piece of excited sealing-wax: if the divergence *increases*, it is the same as that of the wax or *negative*; if it *diminishes*, it is opposite to that of the wax, or *positive*.



Where a more delicate test of the presence of electricity is required, we substitute for the pith-balls two small slips of gold-leaf; and as these are apt to be deranged by the slightest motion of the air, it is necessary to enclose them in a glass cylinder, sufficiently capacious to allow of their divergence. They are connected with the brass cap of the instrument, which is used in the same way as the preceding. This is commonly called *Bennet's gold-leaf electrometer*.

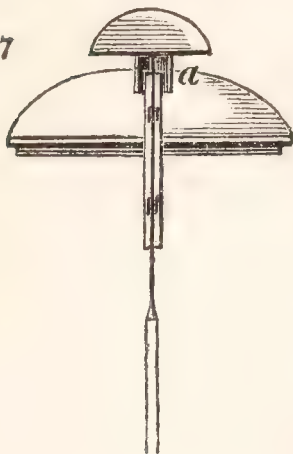


* It will appear hereafter that all substances may conduct electricity, and that the terms conduction and non-conduction therefore are so far incorrect; in em-

ploying them as above we refer to their common acceptance. See, in reference to this subject, FARADAY'S *Experimental Researches*, § 1320 and 1326.

The delicacy of the gold-leaf electrometer is increased by an improvement in the insulation of the leaves, which we owe to the late Mr. Singer. The instrument is constructed, as usual, with a glass cylinder surmounted by a brass cap, but the insulation is made to depend upon a glass tube, about four inches long, and one-fourth of an inch internal diameter, covered both on the inside and outside with sealing-wax or lac varnish, and having a brass wire of a sixteenth or twelfth of an inch thick, and five inches long, passing through its axis, so as to be perfectly free from contact with any part of the tube, in the middle of which it is fixed by a plug of silk, which keeps it concentric with the internal diameter of the tube. *a* is a brass cap screwed upon the upper part of this wire; it serves to limit the atmosphere from free contact with the outside of the tube, and also defends its inside from dust; to the lower part of the wire the gold-leaves are attached, and the whole mounted as usual, as represented, in section, by fig. 127.

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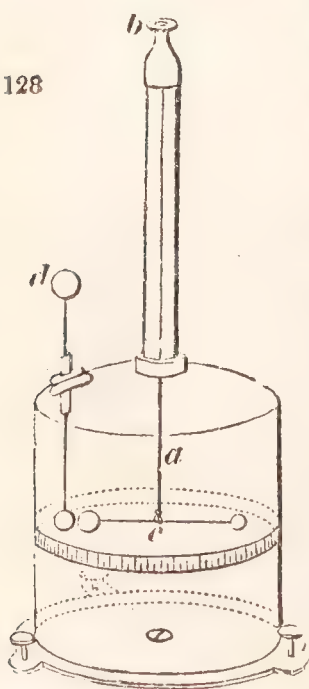


When a gold-leaf electrometer is to be employed in atmospherical investigations, the contrivance described by Mr. Ronalds (*Quart. Journ.*, ii. 249,) may be conveniently applied to it.

The *kind of electricity* by which the gold leaves are diverged may be judged of, as before, by approaching the cap of the instrument with a stick of excited sealing-wax: if it be *negative*, the divergence will increase; if *positive*, the leaves will collapse; upon the principle of the mutual annihilation of the opposite electricities; or that bodies similarly electrified repel each other, but that when dissimilarly electrified they become mutually attractive.

To ascertain the actual repulsive and attractive powers appertaining to weakly-electrified bodies, Coulomb availed himself of the principle of torsion, and thus constructed his *electrical balance*. It consists of a fine metallic wire, *a*, fig. 128, one end of which is attached to the screw *b*, and to the other is suspended the horizontal needle *c*, composed of gum-lac or other non-conductor, and armed at one extremity with a gilt pith-ball, counterpoised at the other end by an index. The conductor *d* is a small wire with a ball at each end, passing through the glass receiver in which the needle is suspended, and having its lower ball opposed to that of the needle. By the screw *b*, the two balls are brought into contact, and the index then points to 0° , on the divided scale of degrees. On communicating a very feeble electrical power to the conductor, it transfers it to the moveable pith-ball, and *repels* it a certain number of degrees, proportional to the intensity of the acquired electricity, and measured by the power of torsion which it exerts

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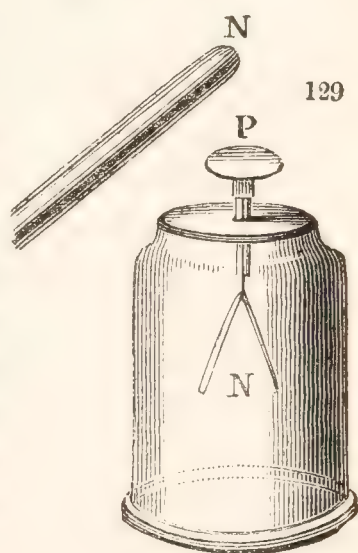


upon the fine wire. By experiments made with this electrometer, it would appear that the electrical powers follow the law of gravitation, in being *in the inverse ratio of the squares of the distances of the acting bodies*. In the most delicate construction of the instrument, a

single silk-worm's thread or a filament of spun glass is used instead of the wire.

By means of the gold-leaf electrometer, constructed as above, we discover the existence of very slight states of electrical excitation, which elude all common methods of detection. If the cap of the instrument be gently struck with a silk handkerchief, a powerful divergence may be given to the leaves, resulting from the friction of the metal and silk; if blown upon by a pair of bellows, electrical excitation is also indicated, depending probably upon the friction of the air upon the metal; and it will be found in the sequel, that we conveniently avail ourselves of this instrument to detect the evolution of electricity in a variety of other cases.

To determine the kind of electricity by which the leaves are repelled, we approach them, as before directed, either with an excited stick of sealing-wax, or a glass rod; if the divergence is increased by the former, it is *negative*; if diminished, *positive*; if increased by the glass, it is *positive*; if diminished, *negative*. In consequence of the law of excitation by induction (see the next section) it is sometimes supposed that this method of merely *approximating* the instrument, instead of actually touching it by the excited wax or glass, might lead to erroneous conclusions; but if we examine a little more particularly into the state of things, we shall find that, consistently with that law, *electro polarity* will be produced, and that consequently, the *gold leaves* will acquire the *same* electricity as that of the wax or glass, although the surface of the brass plate or cap of the instrument, immediately opposed to the wax or glass, may be in an opposite state. Thus, let *N* (fig. 129) represent a piece of excited wax, *negative*; then *P* the cap of the electrometer, will be *positive*; and *N* the gold leaves, *negative*, that is, *similarly* electrified to the wax. The phenomena thus exhibited by this electrometer, are explained as follows by those who advocate the existence of two electric fluids. "When an excited rod is brought over the electroscope, it separates the electricities of the metallic portions of the instrument, attracting the opposite to the upper surface of the cap, and repelling that of the same name into the gold leaves, which being thus excited by the same electricity, repel each other and hence diverge. If the exciting body be $+$, it is the $+$ fluid by which the instrument appears affected; if it be $-$ the leaves diverge from the presence of $-$ electricity. Hence, if when it is under the influence of a glass rod rubbed with silk, a stick of sealing-wax rubbed with flannel be brought near, the divergence diminishes until at last the leaves collapse; the resin having driven down as much negative electricity as there had been positive brought into action by the glass; hence the gold leaves come into their natural and indifferent condition." (KANE.)



§ 4. INDUCED ELECTRICITY.

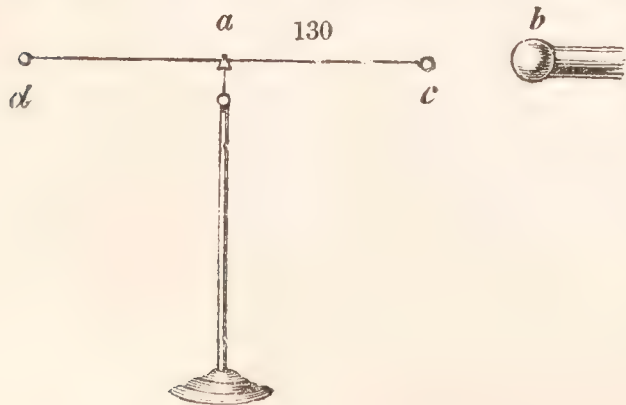
WE have laid it down as a general rule, that no electrical *attractions* exist, except between bodies in *opposite* or *dissimilar* electrical states;

and have shown that when any electrified body, such, for instance, as an excited stick of sealing-wax, is brought near other non-electrified bodies, they have a tendency to mutual attraction. This tendency exists among all surrounding substances; but such, of course, only, as have freedom of motion are observed to move towards the excited electric: such as the suspended feathers, particles of dust, and other light and moveable bodies. Now, as these are *attracted* by the electrified body, it follows that they must previously be thrown into an *opposite* electric state, by the mere *proximity* of the excited electric; and this is really the case: whenever an electrified body is brought near to another in an un-electrified state, that part or surface of the latter which is opposed to the former, becomes *oppositely* electrical, and is consequently *attracted* by it.

Electricity is thus said to be *induced* in the surrounding bodies by the vicinity of any excited electric: so, when a highly-electric cloud hovers over the earth, that portion of the earth's surface opposed to the cloud, becomes in an oppositely electrical state, and consequently attractive of the cloud; thus, during a thunder-storm, we often see an electric cloud perch upon the summit of a hill, and remain there till it has discharged its electricity, when it is wafted quietly away.

Electricity by induction presents many curious phenomena, which may here be stated generally, and more particularly explained afterwards, when induction through glass and other substances will be adverted to. The term *dielectric* has been applied to the air or other medium through which induction takes place, and it will be found that different dielectrics differ considerably in their respective inductive capacities: thus sulphur, lac, glass, and spermaceti have much higher inductive capacities than air.

We have already said, that when an electrified body approaches another which is in its ordinary state, the surface of the latter opposed to the electrified body acquires an opposite state; this opposite electrical state, however, only belongs to the opposed surface; for the other side or end of the body, though also electric, is, (as in the case of the gold leaves of the electrometer represented in the preceding page,) *dissimilarly* so. This statement may be rendered more intelligible by the following diagram: Let *a*, fig. 130, represent a brass needle freely moving upon its centre, which is supported upon a glass foot. *b*, a conductor, *positively* electrified, and within a few inches of the pith-ball *c* attached to one of the points of the needle. We shall now observe that *c* is *attracted* by *b*, and may therefore infer that it is a *negative*; and that this is really the case may be shown by

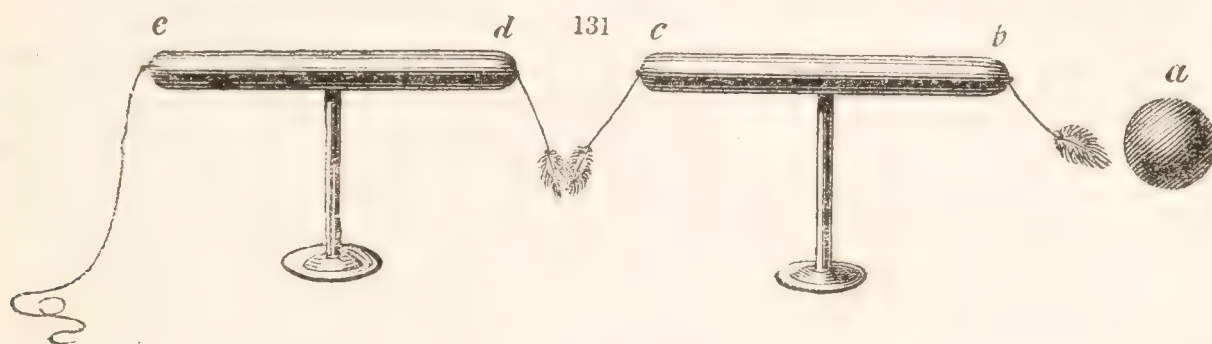


bringing near to the ball *c*, a stick of excited sealing-wax, by which it will be *repelled*. But if we now bring the sealing-wax towards the ball *d*, it will be *attracted* by it: here, then, by the *proximity* of the conductor *b*, we have induced in the needle *a* an *electro-polar* state; *b* being positive, *c* is negative, *d* positive. To explain this further

by the help of our hypothesis: let us suppose the natural or quiescent electricity of *a* to be disturbed by the presence of *b*, which causes a por-

tion of it to be repelled or driven from *c* to *d*. The end *c*, therefore, is *negative* or *minus*, that is, it has *less* than its natural portion of electricity; and *d* is *positive*, or *plus*, because in it electricity is *accumulated*; in the centre *a* there will be a neutral point, in which no electricity is manifest. The state of the needle, therefore, is such, that negative electricity is accumulated at *c* and positive at *d*, and that they each gradually decrease towards the centre *a*. On the removal of the disturbing body *b*, the needle reverts to its ordinary state; or, in other words, the electrical equilibrium is restored.

The *polar arrangement* thus caused by induced electricity, may be carried to any extent: thus, suppose *a* in the following diagram, fig. 131, to represent a body *negatively* electrified, *b* would become positive, *c* negative, *d* positive, *e* negative, and so on, through any extent of conductors, the last being in communication with the earth. Thus the feather attached to the insulated conductor at *b*, is attracted towards *a*, and the feather *c* attracted by *d*; these feathers and surfaces being respectively in *oppositely electrical states*.



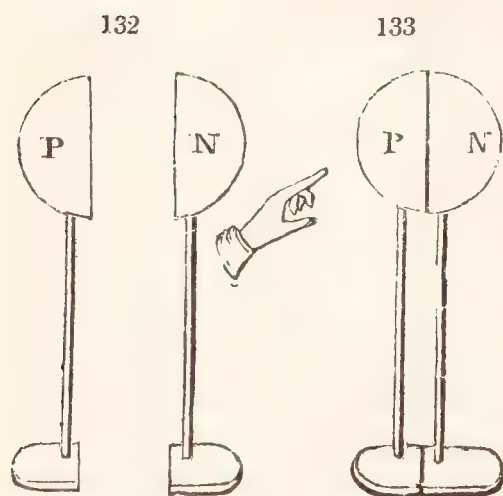
These illustrations will suffice to explain the meaning of the term *induction*, or induced electricity, without a knowledge of which many of the electric phenomena we are about to advert to, would be unintelligible: we shall afterwards find that it presents some very extraordinary consequences in reference to the distribution and accumulation of electricity, and the disturbance of the electrical equilibrium.

The actual electro-polar state of a conductor under induction is well shown as follows: place two gold-leaf electrometers about 18 inches apart, and connect their caps by an insulated wire lying across them; then approach *one* of them with an excited glass tube, which will cause both to diverge; whilst they are in this diverged state, lift off (by a silk thread or insulating handle) the intermediate wire, and at the same time remove the inducing tube, and each electrometer will retain its divergence: on examining that which was nearest to the excited glass tube it will be found *negative*, and that which was at the other extremity of the wire will be *positive*; if we now, by means of a wire with an insulated handle, reconnect the two caps, both electrometers will collapse, and lose all signs of electricity, showing that the negative and positive states were co-equal: a piece of wire with a handle of gum-lac is a convenient connector for the electrometers.

When in these experiments, the conductor electrified by induction is insulated (as it must be to exhibit its polar state), the accumulation of either electricity is of course feeble, being, according to the hypothesis of two fluids, limited to the decomposition of the quantity of neutral electricity contained in it; but if one end of the conductor be connected with

the ground, the supply is comparatively unlimited: this may be well shown by presenting the knuckle or a brass ball held in the hand to the prime conductor of the electrical machine; the opposed surface becomes oppositely electrical by induction, and a succession of sparks pass; but if the person be insulated, the induction is limited, as in the insulated conductor, and only two or three sparks are observed to pass. This passage of sparks, which ensues freely through the intervening stratum of air when an uninsulated conductor is held near a charged conductor, is in all cases the indication of the mutual annihilation of the oppositely electrical states previously established by induction. If the charged conductor be *positive*, it attracts an indefinite quantity of *negative* electricity towards itself, and repels a proportionate or similar quantity of the positive fluid: these opposite *charges* of the opposite surfaces are maintained till they acquire sufficient intensity to upset that peculiar condition of the intervening particles of air upon which induction depends, and then the opposed electricities combine, giving rise to the spark, or disruptive discharge, as will be more fully explained in the ensuing section.

The following experiments on induction are well adapted to class illustration.



Provide two hollow metal hemispheres, or wooden ones covered with tin-foil, each mounted upon a varnished glass stem standing on a wooden foot (fig. 132), so that when placed together they may form the insulated sphere (fig. 133). Having thus placed them, approach them with an excited glass rod, and then remove it. On examining them by a gold-leaf electrometer, they will be found perfectly un-electrified. Repeat the approach of the excited glass rod, and whilst it is retained in its situation, separate the hemispheres

by the removal of one of them by means of the wooden foot, taking care that they remain insulated, and immediately withdraw the excited rod. It will then be found (by the help of the electrometer) that each hemisphere is in an oppositely electrical state as represented by the letters N and P.

If whilst the insulated sphere (fig. 133) is rendered temporarily electrical by induction, it be touched for a moment by the finger, it will be found on first removing the finger, and immediately afterwards, the inducing excited tube, that the globe now retains a negative charge, and will even give a spark, the positive electricity having been carried away by the hand, and not able, therefore, to return, so as to reproduce the neutral state.

On this principle we readily give a permanent *positive* charge to the leaves of the electrometer, by a negatively excited stick of lac. If the excited lac be merely brought near to the insulated cap and leaves, the electro-polar state of the conductor gives a negative divergence to the leaves, entirely dependent on induction, and ceasing on the removal of the lac, as already explained: but if we bring the excited lac near the cap of the instrument (fig. 129), and whilst the leaves are in this electro-polar state of negative divergence, touch the cap P, we immediately

destroy the local polarity of the cap and leaves, and render them positive throughout, and then, on removing the finger from the cap, and at the same time withdrawing the excited lac, a permanent *positive* charge remains in the leaves. If we substitute excited glass for lac, the phenomena are inverted, and the divergence is that of *negative* electricity.

The subject of induction has been acutely studied by Faraday. (*Researches*, Series xi.) Before his researches the phenomena were presumed to depend upon an action taking place in straight lines through non-conducting media, the particles of the medium not being themselves affected; whereas it would appear from his investigations, that "induction is in all cases an action of contiguous particles, consisting in a species of polarity, instead of being an action of either particles or masses at sensible distances;" that it may be propagated not only in straight but in curved lines. Faraday's views upon this question have been so clearly abridged and illustrated by Daniell, that I have availed myself of the following quotation and diagrams from his *Introduction*, in further illustration of this subject.

"We have seen that one electric force cannot be produced without an exactly equal developement of the other; and upon more attentive examination we shall find that no kind of matter, either conducting or non-conducting, is capable of receiving a charge in any way of one kind of electricity independently of the other, or without calling forth an equal amount of the opposite force in adjacent bodies. It was formerly supposed that the electric fluid was confined to the surfaces of bodies by the mechanical pressure of the non-conducting air, in the midst of which all our experiments are carried on; but the fact is, that the electric force originating or appearing at a certain place, is propagated to, or sustained at a distance, through the intervention of the contiguous particles of the air, each of which becomes polarized as in the case of insulated conducting masses, and appears in the inductive body as a force of the same kind exactly equal in amount, but opposite in its direction and tendencies.

"Such a forced arrangement of the molecules cannot be made to appear to the eye in the case of the air, but is established by the most perfect inductive reasoning; and a similar disposition may actually be exhibited by substituting a liquid non-conductor for the air under similar circumstances. If we take a tall, wide-mouthed glass-vessel, and place it upon the prime conductor of the electrical machine, taking care that there may be a good metallic communication through its bottom, and then fill it with spirit of turpentine containing some threads of white silk about one-eighth of an inch in length disseminated through it, they will be little affected upon turning the machine till a metallic conductor is held near the surface of the liquid. Upon presenting, however, such a body, they will immediately erect themselves, and collecting from all parts, will attach themselves to each other end to end, and form a continuous chain from the conductor to the exterior metal, towards which they will always incline as it is moved in different directions. These particles will adhere together with considerable force, as may be felt by touching them with a rod of glass; but the moment the conductor is discharged, they fall upon their sides, and sink to the bottom.

"Now these solid threads of silk accurately represent the fluid particles

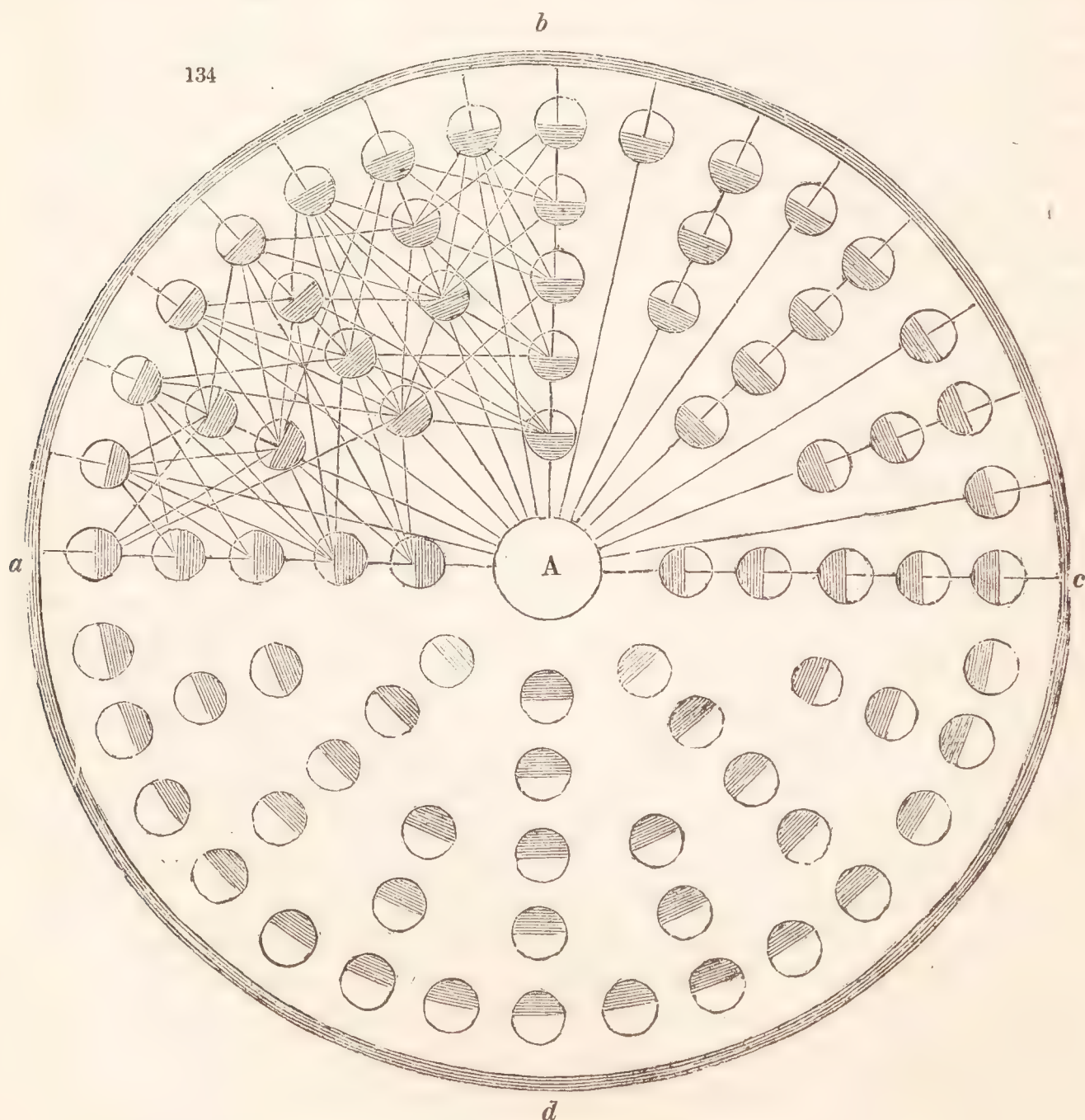
of the spirit in which they float, or of the air which is interposed between a charged conductor and surrounding bodies, and obviously assume a polar state exactly resembling that of insulated conductors in similar circumstances*. If, instead of silk threads, we occasion particles of gold-leaf to float in the spirit of turpentine, the resemblance will be perfect; for, on approaching them with a rod of metal, when the conductor is

* "In the annexed diagram let A represent an insulated electrified ball placed within an insulated metallic sphere, $a b c d$, filled with a non-conducting medium, whose particles are represented by the small included circles. These will be all thrown into a polar state, indicated by the shading, resembling the silk particles in the spirit of turpentine: their dissimilar poles will be all turned towards the ball A, and in this way their combined influence will be thrown upon the metallic sphere, $a b c d$, which will thus have a force of the opposite kind to that upon A, developed upon it, of exactly equal amount, but diffused over the larger surface. Strictly speaking, the sphere itself will be in a

polarized state, but the electricity on its other surface, of the same name as that of the interior ball, will be virtually annihilated by being in metallic communication with the indefinitely large surface of the earth.

"Moreover, the force distributed upon $a b c d$, the quantity of which is just equivalent to that upon A, will be reduced, at any given point, in intensity, in proportion to the square of the distance from the centre of the sphere.

"It is conceived that the polarized particles are capable of affecting each other, not only in straight lines as in the quadrant A b c, but in lines diverging from their centres, as shown in the quadrant A b a."



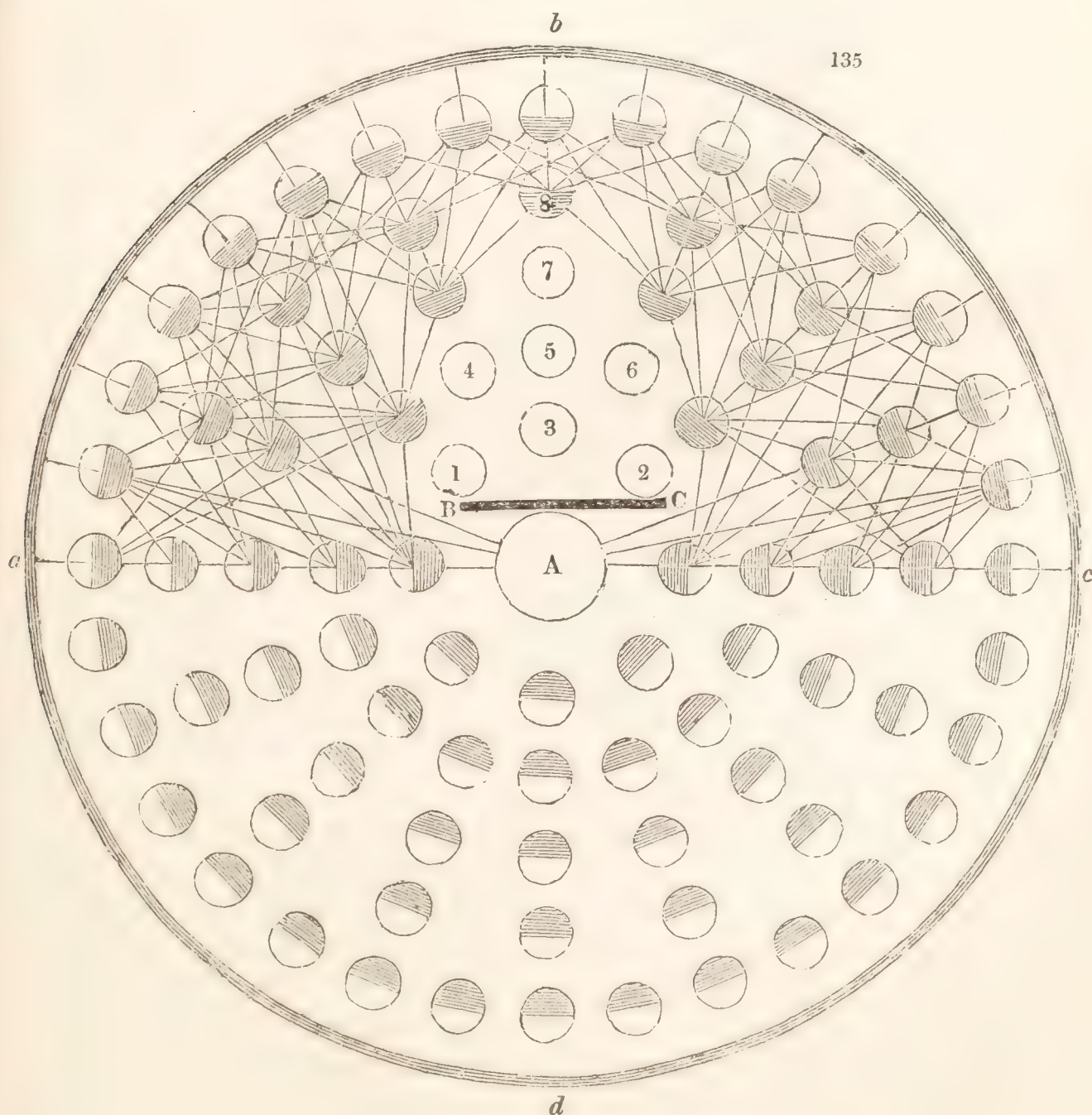
charged, they immediately start on end as if endued with life, assume the polar state, attract each other end to end, but owing to their perfect conduction, discharge their electricity by minute sparks.

“Each polarized particle is in active relation, not only to a line of particles in some definite direction from it, but to all those which are contiguous to it. Hence, there is a lateral diffusion of force, and the lines of inductive action, when unobstructed, tend to spread as from a centre; or may assume a curved direction when any obstacle opposes their free radiation*.”

Faraday has examined the results of the influence of induction through different electrics, with a view of determining their “specific inductive capacities.” These experiments will be noticed further on. (See § 8.)

* “In consequence of the lateral action of the particles upon one another, if *B C* be an obstacle interposed in the course of the induction from *A* to *a b c, d*, the particles 1 2 3 4 5 6 7 will be protected from the influence, but the induction will affect the particle 8, by the bending of the lines of force on each side of it.

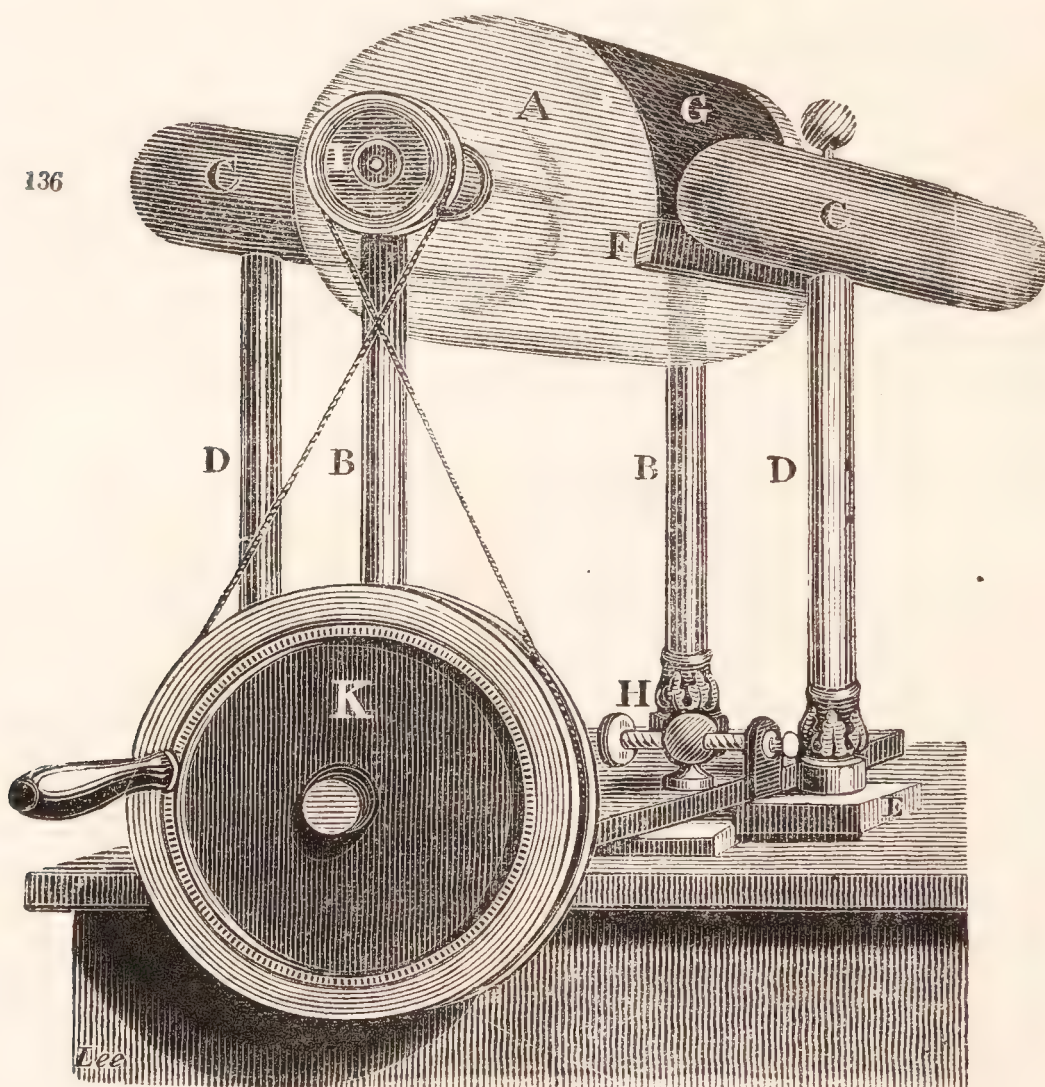
“The particles 1 2 3 4 5 6 7 themselves, although here represented in their natural state, will be affected by a reflex action; but will be polarized to a much lower degree than those within the influence of the direct action.”



§ 5. ELECTRICAL MACHINES.

IN the preceding details we have availed ourselves of the simplest apparatus to explain the leading and principal laws of electrical excitation; all the experiments are easily made, and their results include some of the most important facts connected with the subject, to which, in the sequel; it will be necessary frequently to recur. For the further practical prosecution of these experiments, an *electrical machine* is indispensable; this, therefore, we may now describe.

The best electrical machine for experimental purposes, and for the general use of the student, is represented in the following wood-cut. It is commonly called *Nairne's machine*. (See fig. 136.) It consists of a



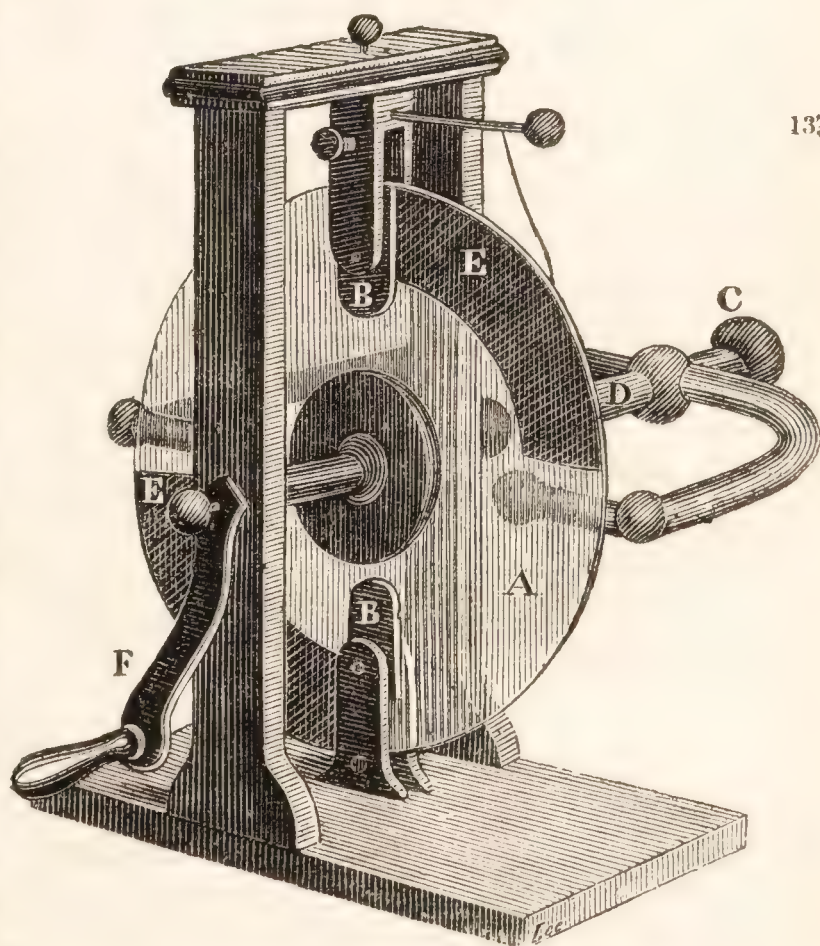
glass cylinder A, about 10 or 12 inches in diameter, and 15 to 20 inches in length, turning between two upright pillars of glass, B B, fixed to a stout mahogany base. Two smooth *metal conductors*, equal in length to the cylinder, and about one-third of its diameter, c c, are placed parallel to it upon the glass pillars D D, which are cemented into the sliding pieces of wood E, by which their distance from the cylinder may be adjusted. One of the conductors has a *cushion*, F, attached to it (by a bent metallic spring) nearly as long as the cylinder, and about one inch or an inch and a half wide, to the upper part of which is sewed a *flap of silk*, G, which should reach from the cushion over the upper surface of the glass cylinder, to within about an inch of a *row of points* attached to the side of the opposite conductor. The conductor to which the cushion is attached is called the *negative* conductor: the other becoming similarly electrical to the glass, and is called the *positive* conductor: H is an adjusting

screw to regulate the pressure of the cushion upon the cylinder. The motion of the cylinder is in the direction of the silk flap, and may be most simply communicated by a handle attached at I, or, if necessary, by the multiplying wheel K. It is obvious, that in this form of the electrical machine, the cylinder and the cushion correspond to the glass tube and silk rubber employed in the former experiments, and that all the phenomena appertaining to the excited *tube* will be exhibited by the cylinder A, and the conductor opposed to it, whilst those of the excited *silk* or rubber, will belong to the cushion F, and to its conductor.

To put this electrical machine into good action, every part should be made *perfectly clean and dry*. The cushion is then anointed with *amalgam*, and applied by a gentle pressure to the cylinder. If *positive* electricity is required, it may be received from the conductor bearing the points, that supporting the cushion being, at the same time, uninsulated by an attached wire, passing from it to the stand; if, on the contrary, *negative* electricity is required, it may be obtained from the insulated cushion and its conductor, the other conductor being uninsulated.

The best *amalgam* is composed of one part of tin and two of zinc melted together, and mixed, while fluid, with six parts of hot mercury in an iron mortar. This mixture is triturated till it becomes a fine powder, which is then formed into a tenacious paste with hogs' lard.

Another form of the electrical machine, usually called the *plate machine*, consists of a circular glass plate A (fig. 137), mounted upon an axis, and rubbed by two pairs of cushions, as shown at BB. The brass conductor C has its points opposed to the plate, and is insulated by the glass stem D: EE are double pieces of oil-silk passing from the cushions to near the points. The whole is supported by a stout mahogany frame, and motion is given to the plate by the winch F.



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These electrical machines have considerable power; they are easily cleaned and excited, and are more portable than the cylinders; but as they cannot be conveniently insulated, the negative electrical power cannot be so well exhibited; for the general purposes therefore of experimental illustration, the former machines are preferable.

When either of these electrical machines have been for some time out of use, they require to be thoroughly cleaned: for this purpose, the conductors and cushions must be removed, and the cylinder or plate cleansed with a little whiting and spirit of wine; it must then be wiped perfectly dry with a clean, warm, and soft cloth. It is a common custom to set the

machines before the fire, but this is apt to soften their cemented joints, and endanger the plate or cylinder; the former especially is often cracked by incautious warming, and, in this case, the crack generally commences at the axis, and gradually proceeds towards the circumference; its progress may often be successfully checked by drilling a hole through the plate at the point of the crack. *Dryness* rather than warmth of the air is requisite for the activity of the electrical machine; it should, therefore, be kept in a dry room. When the glass parts of the machine are perfectly clean and dry, the cushions, freshly amalgamated, may be applied; their pressure upon the cylinder or plate should be moderate, and they also should be dry and warm. The brass parts of the machine and of other electric apparatus are commonly lacquered, which ought not to be, as it often interferes with their uses: the brass knobs especially should be clean and polished, but not varnished.

We are indebted to Mr. Armstrong for another remarkable form of electrical apparatus, which has been called the *hydro-electric machine*. (*Phil. Mag.*, May and July, 1841, and 1843, p. 103.) It consists of an insulated high-pressure boiler, the steam of which is allowed to escape at intervals through a numerous series of peculiarly constructed orifices, and to impinge upon a properly arranged conductor. A fine machine of this description is at the Polytechnic Institution of London: it gives a copious succession of sparks of from 12 to 20 inches in length, and charges a battery of nearly 80 feet of coated glass in 8 or 10 seconds, so that the intensity and quantity of its electricity are both considerable.

It having been observed that water and other fluids during their evaporation from heated surfaces occasionally develop electricity, the source of the electricity of this machine was originally referred to that cause, namely, to the change of state from liquid to vapor. Thus, when a red coal is placed upon the cap of the electroscope, and a little water suffered to dribble upon it, the leaves diverge, and the rising steam is electrical. Faraday, however, has shown the cause of excitation in Armstrong's machine is neither due to evaporation nor condensation, but dependent upon the *friction* of the particles of water which the steam carries forward against the surrounding solid matter of the passage, (*Phil. Trans.*, 1843,) and that the generated electricity is positive as regards the particles of water.

§ 6. GENERAL PHENOMENA OF ELECTRICITY OF TENSION.

WHEN the electrical machine is in good order, and the atmosphere dry, it produces a *crackling noise* when the plate or cylinder is turned, and flashes and *sparks of light* are seen upon various parts of the glass, passing from the cushion to the conductor: if the knuckle be held near the conductor, sparks pass to it through some inches of air, with a peculiar noise, and excite a slightly painful sensation in the part upon which they are received. These, and the other phenomena we may now notice, are especially characteristic of electricity of *tension*.

It is conjectured that the cause of the *spark* thus perceived is the sudden compression of the air or medium through which the electricity passes, and it is always probably attended by a proportionate *elevation of temperature*, as is shown by the power of the spark to inflame spirit of wine, and some other easily inflammable compounds.

In these electrical machines the surface of the glass becomes positive by friction upon the rubber or cushion, which becomes negative; and as the cylinder or plate is kept in progressive motion, it follows that, provided there be a means of carrying off its positive electricity, it will continually receive a new supply from the uninsulated rubber; if, on the contrary, no means of conducting it away be resorted to, it will perpetually annihilate itself by retransmission to the cushion. But when the cushion is insulated, the abduction of electricity must be very limited: hence, to the full and perfect operation of the electrical machine, two circumstances must co-operate; there must be a means of withdrawing the generated electricity from the surface of the glass, and of preserving the supply to the cushion: of these, the former is effected by means of the opposed prime conductor; the latter, by connecting the cushion by a metallic chain or wire with the earth. We accordingly observe, in examining the operation of the electrical machine,—1st, That the electricity in either conductor is extremely feeble when they are both well insulated. 2ndly, That when one conductor is uninsulated, the electricity derivable from the other is proportionately augmented; in the positive conductor, because then the other draws uninterrupted supplies from the earth; and in the negative conductor, because the positive freely transmits, and hence is left in a state rapidly to receive. 3rdly. That the cushion and the surface of the glass are always in opposite states. 4thly, That the negative and positive electricities excited, bear precisely that relation which enables them, when combined, to neutralize each other: in other words, that the *deficiency* of electricity on the one side is exactly such as to be restored by the *redundancy* on the other.

By the aid of Nairne's electrical machine, the phenomena of excitation, and of attraction and repulsion, may be conveniently studied. The conductor attached to the cushion is *negative*, and that opposed to the cylinder *positive*; the former, therefore, represents the *sealing-wax*, and the latter the *glass*, employed in the experiments above described. If we attach two pith-balls to either conductor, they *repel* each other; but if one be attached to the negative, and the other to the positive conductor, they *attract* each other. If the two conductors be connected by a metallic wire or chain, all electrical appearances cease, showing that the negative and positive powers are exactly such as to *neutralize* or *annihilate* each other: and in this case, a current of electricity traverses the wire, passing from the positive to the negative conductor; and, when a break is made in it, a succession of sparks pass between the divided extremities. This wire, during the passage of the electricity through it, exhibits other and most important properties, which we shall afterwards have to advert to.

Those who advocate the hypothesis of two distinct electric fluids explain the action of the electrical machine as follows: they suppose that by friction the neutral electric fluid of the rubber is decomposed, the positive adhering to the glass, and the negative to the surface of the cushion; that the positive surface of the glass in its turn decomposes the neutral electricity of the prime conductor, the negative element of which is attracted by the positive of the glass so as to reproduce upon it the neutral state, whilst the prime conductor having thus lost negative electricity is left more or less highly positive, not by receiving electricity from the revolving glass, but by having parted with its own negative fluid to the glass.

The appearance of the *electric light* is modified by the density of the medium through which it passes. In common air, short sparks are straight, or nearly so, and long ones zigzag: the former are brilliant, especially at their extremities; the latter usually of a paler or redder hue. In condensed air, the electric spark is bright and white; in rarefied air, it is of a reddish tinge, and faint and divided; in the more perfect vacuum of a good air-pump is of a purplish hue, and only visible in a dark room. In a good Torricellian vacuum the light is faint blue; and in the most perfect vacua which can be obtained, it is scarcely visible, and of a greenish tint. In gases, the electric spark usually appears most brilliant in those which are most dense; in hydrogen gas, it is faint and red; in carbonic acid, it is vivid and white. It is also modified by the nature of the surfaces from and to which it passes.

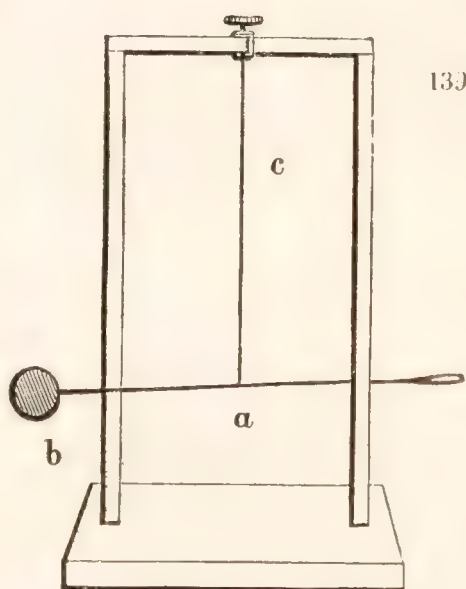
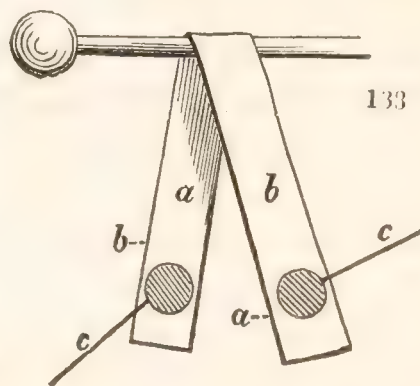
This apparent passage of electricity from one conductor to another, has been termed the *disruptive discharge*: it is the limit of the influence which the *dielectric* (in this instance, the air) exerts in resisting the discharge; and the moment this has taken place, it is assumed that the particles of the dielectric lose their electropolar state, and resume their normal condition.

Whenever therefore a spark passes, it announces the annihilation of the opposite electrical states, they having been previously brought into existence by induction. The knuckle held near the positive conductor becomes negative; and when the opposite states have acquired a certain degree of intensity, a spark passes, and the state of excitation is at an end.

There is an important circumstance attending the distribution of quiescent or *statical* electricity, which is, that it belongs to surfaces only, and is so far independent of quantity or mass of matter, that a hollow sphere receives the same charge as a solid one. Coulomb found that an excited globe of metal afforded no indication of electricity in its interior; and that an excited hollow cylinder, open at the ends, imparted no charge to a small insulated disc, introduced into, and brought into contact with, its interior. The following illustration of the same fact is due to Biot. He suspended a metallic sphere by a silk thread, and exactly covered it by two moveable thin metallic hemispheres, which, by insulating handles, could be applied and removed at pleasure. On communicating a charge to this sphere *with* its exterior coating, he found, upon its removal, that the whole of the charge was carried away upon it, and that the sphere remained without electricity: and again, on charging the sphere, and then applying the coating, the whole of the electricity manifests itself upon the latter, and may again be carried away as before. This experiment requires some dexterity in its performance, but is perfectly satisfactory in its results. In the same way, if any metallic vessel, such as a pail or pot, be insulated and charged with electricity, on bringing an insulated carrier-ball to its exterior, electricity may there be carried away and communicated to a gold-leaf electrometer; but on applying the carrier-ball carefully to its interior, it will not receive a trace of electricity. The cause of this apparent paradox will be evident by a reference to the diagram at page 158. Thus, if we suppose *abcd*, (fig. 134,) to be a hollow sphere charged with electricity, an insulated ball, *a*, introduced into and touching any part of its interior could receive no charge,

“because, being surrounded by a surface in one electrical condition, it could not induce the opposite state by polarising the surrounding air, by which alone a charge could be sustained: this will be at once obvious by supposing the ball, A, shaded the same as the circle, *abcd*, to denote a similar state of electricity, when the polarised state of the particles represented in the diagram will be seen to be impossible.” Faraday well illustrated this condition, by constructing in the middle of a large room, a cubic chamber of twelve feet in the side, in the interior of which no signs of electricity were manifest, although the cube itself was highly charged by connection with a powerful electrical machine, so that large sparks and brushes darted off from its surfaces and angles.

It will now be understood, that what we have termed *electrical repulsion* is only *apparent*, and depends upon attraction by surrounding bodies which act by induction and are dissimilarly electrified: thus the divergence of the gold leaves of the electrometer is occasioned by the absence of all attraction between their opposed surfaces, while they are attracted by the bodies about them. This state of things is well illustrated by attaching a piece of bent tin-plate to the conductor of the electric machine so as to represent the diverged leaves of the electroscope (fig. 138): if we then bring a small disc of gilt paper, *c c*, insulated by a filament of lac, into contact with the outer surfaces *b b*, we shall there find abundance of electricity, but none if the disc be carefully applied to the inner surfaces *a a*, which being similarly electrical and opposed to each other, cannot maintain any charge by induction. The degree and kind of electricity of these discs is easily determined by Coulomb's electrometer, or by a useful substitute for that instrument, made by suspending a delicate rod of lac, *a*, with a gilt paper disc at one of its ends, *b*, by a fine silk or glass filament, *c*, (fig. 139). This disc in its normal state will be attracted by any electrified body, but, if previously rendered *positive*, it will be repelled by a positive and attracted by a negative disc. The small insulated carrier discs, *c* (fig. 138), are very useful in these and similar experiments, and in consequence of the excellent insulating power of lac, the discs will retain the electric state imparted to them for a long time.



It has been concluded that in a solid body, having the form of a sphere, the electric fluid is accumulated in a very thin stratum at its surface, and everywhere equally, so that a spark, taken from any part of the surface, is of equal length, and the electricity has not more tendency to escape from any one part than from any other; its *intensity*, therefore, is said to be everywhere equal. But if we alter the form of the surface, we at the same time alter this equal distribution of electricity. If two similar spheres be placed in contact, there will be two points of greatest

and equal intensity on their opposite sides in a line with their point of contact, and at that point the electricity will be null. In an ellipsoid, also, the greatest accumulation appears at the extremities of the longer axis, and there the *intensity* of the electricity is at its maximum, and increases with the length of the axis: so that if the ellipsoid be considerably elongated, the intensity is very feeble at the equator, and very great at the poles; and in cylindrical bodies, the greater the proportion of the length to the breadth, the greater will be the intensity at the extremities. Coulomb found that in a cylinder, 30 inches long, and 2 inches in diameter, the intensity of the electricity at the ends was to the intensity at the middle as 2·3 to 1. If the conductor be elongated into a point, the intensity there becomes so great as to draw to itself nearly the whole of the electricity; hence, wherever points project beyond the general surface, there is a tendency in the electricity to pass off. The tendency, therefore, of the electric fluid to pass off from surfaces, or in other words its pressure against the air, in the language of the mathematical electricians, is considered proportional to the square of its quantity: so that, if the electric accumulation at four different parts of a conductor be as 1, 2, 3, and 4, the pressure against the air at those parts will be as 1, 4, 9, and 16. "If two balls of unequal diameters be placed together, the maximum intensity of the extreme point of the smaller sphere will be higher than that of the corresponding point of the larger, and by adding a series of balls in contact with each other, all gradually decreasing in size, the intensity will increase upon the smaller as the diameter decreases. We can conceive a succession of such balls gradually diminishing till the series ends in a mere point, at which the electric tension will be at its maximum. In consequence of this law of distribution, a powerful dispersion of electricity takes place from all bodies of a pointed form, the intensity upon them increasing to such an extent that the surrounding insulating medium of air gives way before it, and no longer suffices to restrain it." (DANIELL.)

§ 7. ILLUSTRATIONS OF ELECTRICAL ATTRACTION, REPULSION, AND INDUCTION, AND OF THE INFLUENCE OF POINTS.

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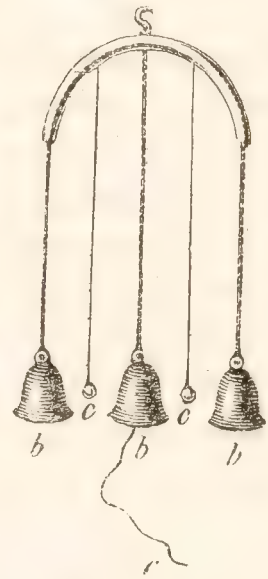
THE statement of facts respecting electrical attraction, repulsion, and induction, admits of many striking illustrations by the electrical machine.

The *head of hair*, which stands on end when electrized, serves to illustrate the direction of the lines of induction, each hair, as if repelled by its neighbour, radiating towards the nearest point in an oppositely induced state, and consequently converging towards the finger when held near them. A similar experiment may be made by placing a person upon an insulated stool, in connexion with the conductor of the electrifying machine; his

hair will diverge as in the above figure. A tassel composed of long strips of tissue paper, and suspended in the centre of a room, is also a good and easy illustration of the lines of induction: when electrised, the

filaments separate, and open out like radii from a centre, and, on approaching them with a conductor, they incline towards it, in consequence of the concentration of force upon the nearest surface.

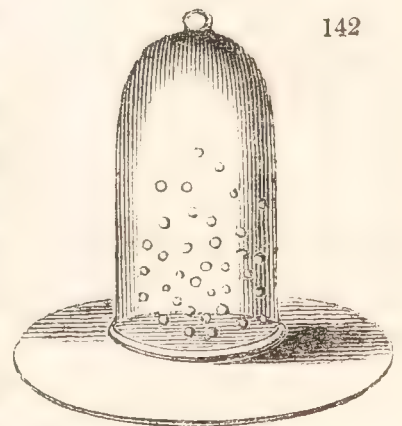
The following is a sketch of the simplest form of the *electrical peal of bells*, which ring by the attractions and repulsions of small clappers suspended between them. The bells are arranged as follows: *a* is a brass hook and wire by which they are suspended to the conductor; *b* the bells attached to the wire by a brass chain, the centre one being suspended by silk; *c* the clappers, also suspended by silk. The electricity received at *a* is slowly dissipated by the edges of the bells, the ringing of which is occasioned by the alternate attractions and repulsions of the insulated clappers. The central bell, which is suspended by silk in the same way as the clappers, is connected with the table by the wire *c*, so as to un-insulate it in that direction.



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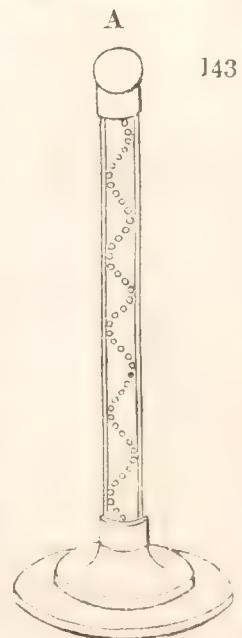
Dancing figures, cut out of light paper, may be made to exhibit very ridiculous movements by a little management in turning the machine. For this purpose, suspend a brass plate from the conductor to the machine, and beneath it, at the distance of four or five inches, place a similar brass plate connected with the ground; on this put the paper figures; when the upper plate is electrified, they rise and perform a dance by their motion between the plates.

A good experiment, illustrating attraction and repulsion, consists in attaching a wire, with a blunt point, to the prime conductor, and holding over it a clean dry bell glass, the interior of which will thus receive a superficial charge; if it be then set upon the table over a dozen pith-balls of different sizes, they will dance up and down in it for several minutes, until they have nearly carried off its redundant electricity.

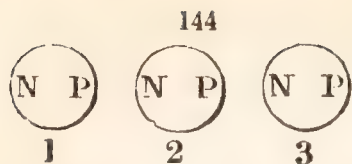


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Among the experiments particularly illustrative of electrical induction, we may notice the *luminous tubes* and *words*, in which a number of sparks are made to pass between small pieces of tin-foil, so arranged as to produce in a darkened room a variety of figures and devices. In the *luminous tube*, a number of small spangles of tin-foil are pasted spirally round a tube about half an inch in diameter, and within a very short distance of each other; upon holding the brass ball *A* to the prime conductor of the machine when in good action, the other end of the tube being uninsulated, a beautiful succession of small sparks is seen between each of the little discs of foil. The opposite electrical states are here produced by induction throughout the series of spangles, the passage of the sparks indicating the momentary annihilation of the electricities. Let the following figures, for instance (fig. 144), represent three of the discs or span-



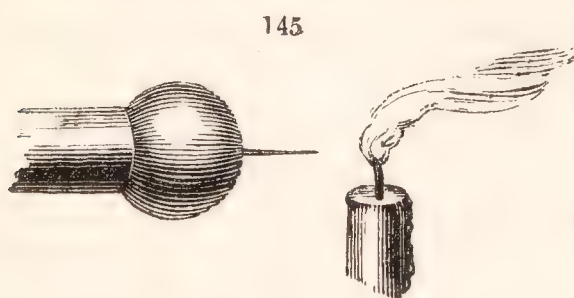
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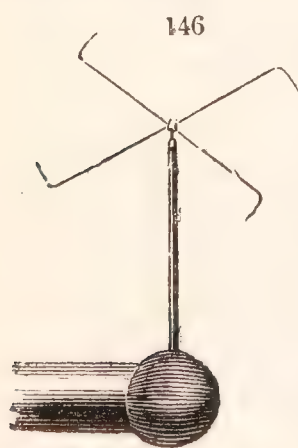
gles: it follows, then, that 1, being held near to the positive conductor, will become *polar*, as represented by the letters N and P: and the whole series, whatever may be their number, will be thrown into the same state as the conductors represented in the figure at page 155, and remain so till the spark passes.

A curious and important phenomenon of induction is presented by an uninsulated wire at the moment of the passage of an electric discharge through it; it acts by induction upon neighbouring bodies, and a small spark may be taken from any part of it. Thus, if a long wire be laid round a room, communicating with good conductors at one end (the gas or water pipes, for instance,) and so arranged with a ball at the other that sparks may be taken in quick succession by it from the prime conductor, it will be found to give off small sparks to any good conductor brought close to any part of its length. It appears, therefore, that although a conductor may be in perfect communication with the earth, it may, nevertheless, so influence neighbouring conductors as to cause lateral discharges.

The influence of points in receiving and carrying off electricity has already been adverted to, and may be further elucidated by the following experiments. If we hold a pointed wire to the prime conductor, it rapidly and silently draws off its electricity, and sparks cannot be taken from it either by the knuckle, or by a brass ball, while the point is in its neigh-



bourhood; or if we attach a pointed wire to the conductor, there is the same convection of electricity; and on holding the hand near the point, we perceive a peculiar coldness, or wind, as it were, which has been called the *electrical aura*: it is even sufficient to blow out a candle held near it. This arises from the secession of the electrified particles of air in consequence of the inductive force concentrated upon the point.



If the point be moveable, it will of course be itself reacted upon, and upon this principle a variety of ingenious apparatus has been constructed, such as *flywheels*, *orreries*, and so on. A simple instance is shown in the annexed cut (fig. 146), in which a *fly* with four arms, each terminating in a point at right angles to the arm, is balanced at its centre upon a pointed wire stuck into the prime conductor. The escape of the electricity from the points, and its action upon the adjacent air, causes the fly to revolve rapidly.



If these experiments be made in the dark, it is observed that a point held towards the *negative* conductor has the appearance of giving out a *brush of light* (fig. 147); but when held to the *positive* conductor, a *luminous star* or point is all that is observed (fig. 148). These appearances have been supposed to demonstrate the existence of an *electric fluid*, which, in the one instance, is supposed to be *escaping from*, and, in the other, *received by*, the point: but these

affections of light cannot be admitted as proofs of the existence of any distinct form of matter.

The philosophy of the electric discharge by sparks, brushes, &c., has been minutely studied and ably illustrated by Faraday, more especially in the twelfth Series of his *Researches*: he has also described its appearance in various media or dielectrics; his details upon these subjects are extremely curious and important, but are too extended to be here quoted, and scarcely admit of such abridgment as to bring them within my limits; I must, therefore, content myself by referring the reader to the original. It will be observed that the brush differs from the spark in being “a discharge between a bad or a non-conductor, and either a conductor or another non-conductor; the *spark* ensues where an insulating dielectric is interposed between two conducting surfaces in opposite states of electricity; and then if the actions be continually increased in strength, or otherwise favoured, either by exalting the electric state of the conductors, or bringing them nearer each other, or diminishing the density of the dielectric, a *spark* at last appears, and the two forces are for the time annihilated, for the discharge has occurred.”

§ 8. OF INDUCTION THROUGH GLASS, AND OF THE LEYDEN JAR.

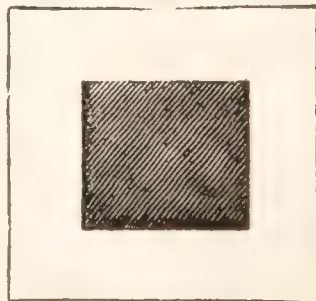
FROM what has been said respecting *induced electricity*, and the electrical accumulation dependent upon it, it will appear that the intervention of conductors and non-conductors, or imperfect conductors, is requisite to the existence of the phenomena. In the cases cited, the non-conducting medium through which it takes place, or the dielectric, is the *air*; we shall now show that induction may also take place through *glass*.

For this purpose it is only necessary to excite one side of a clean, dry pane of glass, by rubbing it with a piece of silk; and, on holding a feather or pith-ball to the other side of the pane, it also will be found electrical. If we now examine the nature of the electricities by which the glass plate is charged, it will be found that the rubbed side being *positive*, the opposite side is *negative*.

In the same way we may charge a plate of glass with the opposite electricities, by holding it to the prime conductor of the machine: in this case sparks will often appear to pass through the glass; but, on removing it, the side which has *touched the conductor* will be found *positive*, and the opposite side *negative*.

As glass is a non-conductor, it is difficult to spread the electricity equally over its surface: this, however, may easily be effected by coating both sides of the pane with thin tin-foil to within about an inch and a half or two inches of the edge, as shown in fig. 149. If we now communicate electricity to one side of the plate, the other, not being insulated, will become oppositely electrical, and in this way a *charge* will be acquired by the plate: if we now, by means of a bent wire, make a communication between the two sides of the coated pane, a bright spark will pass, and the accumulated electricities will be immediately annihilated.

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We avail ourselves of arrangements of this sort for the purpose of accumulating electricity, which may thus be accomplished to a great and

powerful extent; but the pane of glass is an inconvenient form of apparatus for the purpose, and we usually substitute for it a phial or jar, as represented in fig. 150, coated inside and out with tin-foil to within three or four inches of its mouth. A brass wire surmounted by a knob, is then made to communicate with the interior coating, and the apparatus is ready to receive its charge of electricity, precisely upon the same principle as the pane of glass. This is called the *Leyden jar or phial*, the method of arrangement having been accidentally discovered in 1743, by Cuneus and Muschenbroek, of that University. The glass should be thin, and, as far as possible, uniform throughout; for phials or jars which are very thick, or much thicker in one place than another, are unfit for the purpose. (*Hist. de l'Académie*, 1746, p. 1).

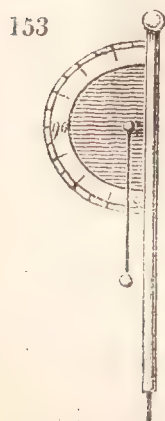
If we now hold the jar by its outer coating, and present the knob near to the conductor of the machine, a succession of sparks will pass into it, at first very rapidly, afterwards more slowly, and at length ceasing altogether. The jar is then *charged*; and if a communication be now made by a metallic wire, from the outer to the inner coating, a bright spark, attended by a snapping noise, will pass from the knob, after which no further effect will be produced, the jar having been *discharged*. The jar may also be charged by receiving the sparks upon the outer coating, whilst the knob is held in the hand.



The wire used for the above purpose should be mounted with balls at its ends, and is usually called a *discharger*, *a*; it is sometimes *jointed*, for the convenience of applying it to large and small jars, and mounted upon a glass handle, *b* (figs. 151, 152).

If, having charged the jar, and holding its exterior coating in one hand, we touch the knob with the other, the spark passes as before, and we perceive a peculiar and very painful sensation at the wrist and elbows, and across the breast, which is called the *electric shock*. It is painful for the moment only, and leaves little other permanent impression than that resulting from fear or surprise.

In charging the jar as above described, if we keep it in contact with the conductor, and the machine is in good action, we observe, after a time, that flashes of light pass across the uncoated interval, which are soon followed by a loud crack or explosion, and a long and brilliant spark passes from the wire to the coating. In this case the electricity has been accumulated to such a degree of intensity as to discharge itself spontaneously over the exterior uncoated interval.



To ascertain the relative charge which the jar has received, and its power of retaining the charge, we employ the *quadrant electrometer*, (fig. 153,) contrived by Henley. It consists of a round stem of metal, seven or eight inches long, surmounted by a ball, to which is attached a semicircle, most conveniently made of thin ivory: in its centre a pin is fixed, on which a slender slip of cane, about four inches long, with a pith-ball at its other end,

turns freely, and traverses the semicircle as an index; the lower half of the semicircle is divided at the edge into ninety degrees. When this instrument is electrified, there is, of course, a tendency to repulsion between the moveable ball and the stem: the ball therefore recedes, and carries the index over the graduated circle, to a greater or less extent, in proportion to the intensity of the electric charge. The repulsion is at its maximum when the index stands at right angles to the stem, or at 90° upon the scale. This electrometer may be fixed upon the prime conductor, or upon the knob of the jar. The latter is often a very convenient place for it, because, having charged the jar and removed it from the conductor, we see by the behaviour of the electrometer how far the jar retains its charge.

There are many other electrometers which are applicable to these high charges of electricity, among which Cuthbertson's *Balance Electrometer*, and Lane's *Discharging Electrometer*, will be found very useful. Mr. Harris, of Plymouth, has also described a balance electrometer, (*Phil. Trans.*, 1834, p. 213,) by which the mutual attraction of oppositely electrified surfaces may be very accurately estimated and compared; and in experiments in which it is required to charge Leyden jars or batteries with known proportions of electricity, the *unit-jar*, contrived by the same electrician, is also a most useful piece of apparatus.

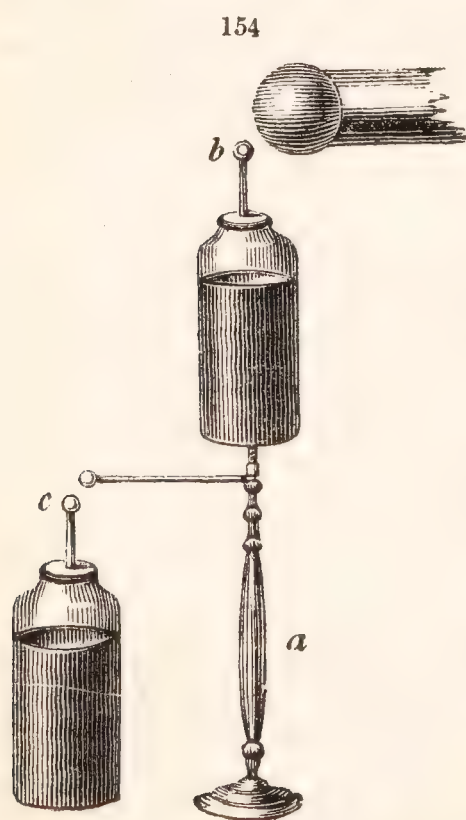
In charging the Leyden jar many hundred sparks are observed to enter it, which, when it is discharged, are all concentrated into one; hence the brilliancy of its light, the loudness of the explosion, and the acuteness of the sensation which it produces.

When the jar is in direct communication with the conductor of the machine, it diminishes the intensity of its electricity, and consequently admits of a greater change in its electric state before any given resistance is overcome, or force of attraction manifested. This is shown by attaching the quadrant electrometer to the conductor of the machine, which, when turned, immediately causes it to rise to its full extent; but when the interior coating of the jar is in union with the conductor, the machine must be turned for some time before the rise of the electrometer attains its maximum.

The *annihilation* of *positive* by *negative* electricity, and the reverse, may be strikingly shown by attaching the quadrant electrometer to a Leyden jar, and giving it a certain charge—say to twenty degrees—from the *positive* conductor; then transfer it to the *negative* conductor, and whilst apparently receiving a negative charge, the electrometer will gradually fall, and, at length, all electrical accumulation disappear: then, as the jar acquires its negative charge, it will again rise, and may be again discharged by transferring it to the positive conductor.

The power of the Leyden phial, as a source of electrical accumulation, being dependent upon the opposite states of its two surfaces, it is obvious that one of them must always be connected with the ground, in order that it may acquire its charge. If we suspend a jar by its knob (a thin globular jar answers best for this experiment) to the positive conductor of the machine, its outer coating, being surrounded by dry air, cannot give off any of its electricity, and consequently it will receive no charge so long as it remains thus insulated; but if we hold the hand near the outer coating, sparks of positive electricity will pass off

and the jar acquire a charge. This is a good experiment, illustrating the Franklinian theory of electricity, which supposes the electric fluid to be present in all bodies, but to manifest itself only when its equilibrium is disturbed. Thus, when we charge a jar in the usual way, we *add* to the electricity of its interior coating, whilst its exterior *throws off* an equivalent quantity: so that the former becomes *positive*, or *plus*, and the latter *negative*, or *minus*; but if the jar be *insulated*, the electricity cannot escape from the outer coating, and consequently the jar cannot be charged. The theory of two fluids assumes that the positive electricity deposited upon the inner surface of the jar repels the positive electricity from the outer surface of the jar, and attracts the negative electricity: that, therefore, every spark which passes from the conductor to the knob, occasions an increase of positive electricity upon the inner surface, and of negative electricity upon the outer surface, and that the mutual attraction between these two electricities prevents their spontaneous escape, and occasions a greater accumulation of each upon their respective surfaces: that when a communication by a perfect conductor is made between the two surfaces, the electricities rush into combination, and all appearances of accumulation or excitation are at an end.



The following experiment further illustrates this subject: Take two Leyden jars of similar size (fig. 154); insulate one of them by fixing it upon a glass stand, *a*, and place the other on the table, with its knob half an inch distant from the coating of the insulated jar, the knob of which should be placed at the same distance from the conductor of the machine. For every spark that passes to the knob of the first jar, *b*, there will be a similar spark pass *from* its coating to the knob of the second jar, *c*, and both jars will become *similarly* and equally charged. As, therefore, the second jar is thus charged by sparks emitted from the exterior surface of the first, and as their charges are equal, it follows that for every portion of electricity *added* to one side of the coated glass, a corresponding or equivalent portion *leaves*

the opposite surface. The preceding wood-cut shows the proper arrangement of the apparatus for this experiment.

Upon this principle a jar may be charged by the transfer of its own natural electricity from one surface to the other: for instance, suspend a jar to the *positive* conductor of Nairne's machine, and connect its *outer* coating by a wire with the *negative* conductor or rubber, the whole being in a state of insulation, so as to prevent the access of electricity from the earth. A few turns of the machine will charge the jar; that is, the electricity which is thrown *into* its inner surface by the positive conductor, is abstracted *from* its outer surface.

This experiment is further instructive, as showing the *impermeability* of glass to the electric fluid, for the conductor and the rubber of the

machine are separated from conducting contact with each other by the thickness of the glass jar only, and a considerable accumulation of electricity takes place, which the contact of the thinnest film of conducting matter, or the slightest fissure in the glass, would effectually prevent. When the glass of the Leyden jar is very thin, it does occasionally happen that it is perforated by a powerful charge; in this case a small round hole is observed in the glass, and the jar is rendered useless.

It has been said above, that a plate of glass not covered by tin-foil, may be charged by contact with the prime conductor: *the metallic coating, therefore, is not essential to its charge*, but its principal use is, by its conducting power, to spread the electricity over the surface of the glass, and to enable it, when the discharge is made by uniting the opposite surfaces, to be carried off *at once* in a single spark. Jars are sometimes made with moveable coatings; these may be charged as usual, and the coating removed and again replaced, when it will be found that they still retain their electricity, which belongs in fact to the molecules of the glass.

Faraday's researches have disclosed new views respecting the extraordinary condition of the glass, or of the molecules of the glass in a charged jar, and as constituting the polar *dielectric*; each layer of particles being, as he assumes, thrown into a peculiar polar condition, which, if retained, constitutes insulation, but which, if lowered by the communication of power from one particle to another, constitutes conduction: he regards insulation and conduction as only extreme degrees of one common condition or effect, and shows that these two apparently perfectly dissimilar conditions may be associated by numerous intermediate links. (See Ser. xii. of his *Researches*.)

The following experiment to a certain extent illustrates the condition of the charged glass in the above experiments; if we apply to particles what we here observe in regard to masses. Apply the uncoated sides of two thin plates of glass, each coated upon one side only, to each other, and charge them; on attempting to separate them, they are found to adhere together, and, on separating them, the uncoated side of the plate which had touched the conductors will be found positive, and that of the other negative.

Faraday's views of the nature of induction led him to infer the existence of a *specific inductive power* peculiar to each substance, and he proved it by very decisive experiments (*Researches*, Ser. xi.), in which, among other forms of apparatus, he employed what he has termed a *differential inductometer*, one of the forms of which consisted of two insulated brass plates placed within a certain distance of each other, one of which was connected with the cap of a gold-leaf electrometer: on electrifying the other, it acted by induction through the air upon the electrometer, and produced a certain extent of divergence of the leaves: plates of different substances were then substituted for the air interposed between the plates, and the divergence was either increased or diminished according to the relative facilities with which induction took place through the interposed substances: he thus ascertained that the specific inductive capacity of air being assumed as = 100, that of glass is = 176, of shell-lac = 200, and of sulphur = 224. With respect to aëriiform bodies, he ascertained the curious fact that they all possess the same power of sustaining induction; no variations, either of their density or elasticity,

produced any change in the electric tension, till rarefaction was carried so far as to enable the discharge to take place across them; hot and cold, and dry and damp air were compared, but no difference was observed.

In speaking of the different states of electricity, the terms *quantity* and *intensity* are frequently used to indicate the different phenomena which it exhibits: the former implies the actual quantity of electricity in any body; and the latter, or the term *tension*, signifies the state of electricity indicated by the electrometer, and its power of flying off from surfaces, and passing through a certain stratum of air or other dielectric. The meaning of these terms will be more evident when we are considering the electricity of voltaic combinations: in the mean time, as regards the electricity of the machine, they may, perhaps, be further illustrated as follows: If we suppose a charged Leyden phial to furnish a spark, when discharged, of one inch in length, we should find that another uncharged Leyden phial, the inner and outer coating of which were communicated with those of the former, would, upon the same quantity of electricity being thrown in, reduce the length of the spark to half an inch: here, the *quantity* of electricity remaining the same, its *intensity* is diminished by one-half, by its distribution over the larger surface. Upon the same principle, if a long metallic riband be coiled up and placed upon the cap of a gold-leaf electrometer, the leaves of which are fully diverged by a sufficient charge of electricity, it will be found upon uncoiling the riband by means of an attached silk thread, so as still to preserve insulation, that the leaves collapse to a greater or less extent, in proportion to the quantity of the riband uncoiled, and that, upon allowing it again to coil up, they again diverge; here the extent of the divergence is proportionate to the intensity of the electricity, which, the quantity remaining the same, is increased or diminished inversely as the surface exposed.

It is obvious, that the *extension of surface* will be attended with a greater superficial exposure to the unelectrified air; and hence it might be expected, that a similar diminution of intensity would result from the vicinity of the electrified surface to the ground, or to any other body of sufficient magnitude in its ordinary or unexcited state. That this is the case, may be shown by diverging the leaves of the gold-leaf electrometer, and in that state, approaching the instrument with an uninsulated metallic plate, which, when within half an inch of the electrometer-plate, will cause the leaves to collapse; but on removing the uninsulated plate, they will again diverge, in consequence of the electricity regaining its former intensity. The same fact is shown by the *condensing electrometer*.

The supposed influence of the air upon the retention of electricity by surfaces has already been mentioned, and it has been stated in illustration of it, that the Leyden phial, if charged, and placed under the receiver of the air-pump, gradually loses its charge during exhaustion, and that if the experiment be made in the dark, the two electricities are seen annihilating each other by flashes of light. This tendency of electricity to fly off from surfaces, has been represented as greater in rare than in dense media, and consequently the length of the spark, or *striking distance*, (as when a charged jar is discharged,) supposing the *quantity* of electricity to remain constant, will vary inversely as the density of the air; and, according to Harris, the resistance to the passage of the charge varies as the

square of the density of the air; and Dr. Turner found the striking distance for the same charge greater in hydrogen than in air, and greater in air than in carbonic acid gas.

The passage of electricity through air of different densities, and in vessels and tubes of different shapes, lengths, and diameters, gives rise to a number of beautiful and very interesting experiments. The good conducting power of flame, and the facility with which it discharges electricity, may also probably be referred to its rarity. But such phenomena, and others which have been more exclusively referred to the air's pressure, are principally referable to changes in the inducing power of the dielectric, or surrounding medium, and are perfectly consistent with those views of the nature of specific induction which Faraday has deduced from his experimental researches. (Series xii.) In reference to the pressure of the atmosphere, as influencing the retention of electricity upon the surfaces of conductors, he remarks, that "it associates two such dissimilar things as the ponderous air and the subtle and even hypothetical fluid or fluids of electricity by gross mechanical relations; by the bonds of mere static pressure. My theory, on the contrary, sets out at once by connecting the electric forces with the particles of matter; it derives all its proofs, and even its origin, in the first instance, from experiment; and then, without any further assumption, seems to offer at once a full explanation of those and many other singular, peculiar, and, I think, heretofore unconnected effects."

The Leyden jar furnishes a striking illustration of that case of induction before alluded to, in which the two electric forces are so limited in their direction as to present no indications external to the apparatus employed; thus, if we charge a jar, and then, by an insulated handle or silk thread, remove the charging ball and wire, such jar will present no electric appearances on examining either coat by an insulated carrier-ball; if such a ball, having been in contact either with the inner or outer coat, be examined by the gold-leaf electrometer, no signs of electricity can be detected: the two forces are confined to the coatings, or to the particles of the dielectric contiguous to them, and are entirely engaged to each other by induction through the glass. But if we now replace the charging-ball and rod, by an attached silk thread, then the part projecting above the jar will give a powerful charge to the carrier-ball, and the outside coating of the jar, if it be insulated, will be found in the opposite state; each strongly inductive to surrounding objects; and after these trials, on discharging the jar, we have evidence, by the usual phenomena, of the annihilation of the previous inductive state. (FARADAY, Ser. xiv., § 1682.)

The power of the Leyden jar, in receiving and retaining electricity, is proportioned to its surface, but a very large jar is inconvenient, and difficult to procure; the same end is attained by arranging several jars, so that by a communication existing between all their interior coatings, their exteriors being also united, they may be charged and discharged as one jar. Such a combination is called an electrical *battery*, and is useful for exhibiting the effect of accumulated electricity. The jars are usually arranged in a wooden box or case coated on the inside with tinfoil, upon which they rest, and their knobs are connected by rods so arranged as to admit of two or three, or of the whole battery being simultaneously charged, batteries usually including either nine or twelve jars.

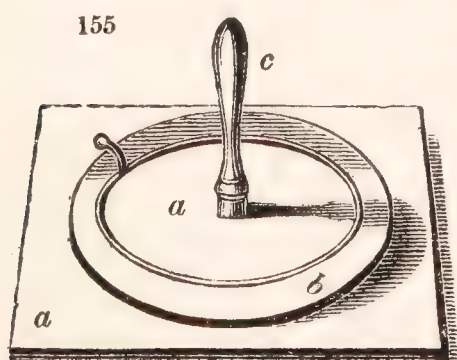
The discharge of the battery is attended by bright light, and by a considerable report, and if it be passed through small animals it kills them; if through fine metallic wires, they are ignited, melted, and burned; and gunpowder, cotton sprinkled with powdered resin, and a variety of other combustibles, may be inflamed by the same means.

The mechanical force that accompanies the electric discharge is shown by the perforation of paper, the tearing of the leaves of plants, and of pieces of wood, and the breaking of plates of glass, through or over which it is made to pass; chemical decompositions may be effected by it, and it produces magnetic effects consistent with the laws which we shall afterwards point out*.

We observe, therefore, that certain attractive, repulsive, and inductive powers belong to electricity in a quiescent state (*Statical Electricity*), and that when in motion, it produces heat, light, chemical effects, and magnetism (*Dynamic Electricity*). Of this production of heat and light many cases have already been cited: in illustration of the chemical power, a current of electricity may be made to pass through a piece of paper moistened with solution of iodide of potassium, when iodine will be evolved, forming a brown spot at the point of the entrance of the current: and in reference to the production of magnetism, if a steel needle be attached at right angles to a wire through which the battery is discharged, it will be found to have acquired polarity. These effects of the electric current, as produced by the common machine (frictional electricity), are merely here cited in reference to their more full development hereafter, and their connexion with the phenomena of voltaic or chemical electricity.

§ 9. OF THE ELECTROPHORUS, AND CONDENSER.

THE *electrophorus* (fig. 155) is often used as a permanent source of electricity, and may sometimes be conveniently and economically substituted for the electrical machine, especially in the chemical laboratory.



It consists of two *metallic* plates, *a a*, with an intervening plate of *resinous* matter, *b*; for the latter equal parts of shell-lac, resin, and Venice turpentine are generally used, the mixture being carefully melted in a pipkin, and poured, whilst liquid, into a wooden or metal hoop, of a proper size, placed upon a polished surface of glass or marble, from which it easily separates when

* The intensity of the heat produced even by the common electric spark, is such as easily to inflame alcohol, kindle gas flames, and so on; the reason why this heat is not, in common cases, observed, is the excessive rapidity of the effect, of which, as appears from Wheatstone's experiments, the term *instantaneous* gives us but a very imperfect idea; hence it is, that the spark taken from the hand *has not time to burn*, though a succession of sparks limited to the same spot produces inflammation; and we shall afterwards find, that by dimi-

nishing the rapidity of the progress of electricity, or using a continuous current, we get a variety of effects *completed*, of which the excessive transiency of the common electric spark, either from the machine or Leyden jar, prevents the accomplishment. Any continuous current of electricity, which we can obtain by the common machine, is extremely small in *quantity*, hence the difference between its effects and those which we shall afterwards witness in other cases of electrical excitation.

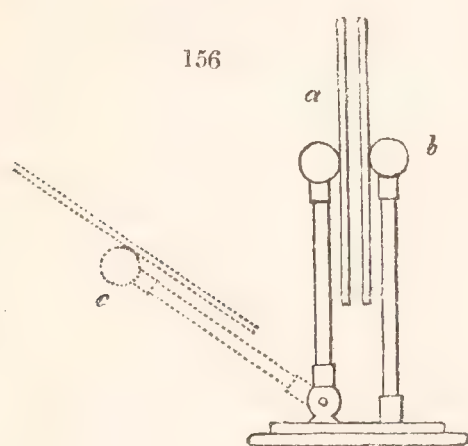
cold; it should be about half an inch thick, and the smooth surface being uppermost, the lower side should be covered with tin-foil, or attached to any other metallic plate; a smooth but unvarnished brass plate, with a glass handle *c* attached to it, is then placed upon the upper surface of the resinous plate, and of rather smaller diameter. The resin having been previously excited by gentle friction with a piece of dry fur, the instrument will be found to exhibit the following phenomena.

Upon raising the brass plate by its insulating handle, it will be found very feebly electrical; replace it, touch it with the finger, and again lift it off by its handle, and it will give a spark of *positive* electricity. This process may be very often repeated without fresh excitation, which circumstance, as well as the nature of the electrical charge, shows that the electricity of the moveable brass plate is not *directly* derived from the resin, but that it depends upon *induction*: this will perhaps be more obvious by considering the upper plate, not as in absolute contact with, but merely very near the resinous disc, which, from the minute irregularities upon its surface, is really the case: the negative electricity, therefore, of the excited resinous plate, is communicated from a few points of contact to the brass plate, upon its first application, and then, the latter is precisely in the state of a conductor opposed to, but not touching, an electrified surface; and, consequently, in due condition to be rendered permanently electrical by induction, when occasionally uninsulated by the contact of the finger. The brass plate, when placed upon the resin, may, in fact, be regarded as in a polar state; the lower surface near the resin being *positive*, the upper surface being *negative*. Upon touching the upper surface with the finger, it instantly *acquires* electricity, loses its apparent polarity, and becomes positive, giving, upon removal, a positive spark to any conductor. It is obvious that in this case the brass plate represents one end of a conductor of indefinite extent. That the quantity of electricity received by the plate is equivalent to that given out, is supposed to be shown by the following experiment: Place the metallic upon the resinous plate, and touch the former with the knob of a Leyden phial; then touch the cap of an electrometer with the knob of the phial, and it will give a certain *negative* divergence to the leaves; raise the plate and present the knob of the jar to it, a spark will pass; and, upon applying the jar a second time to the electrometer, the leaves will collapse, showing the annihilation of the former negative by the latter *positive* charge.

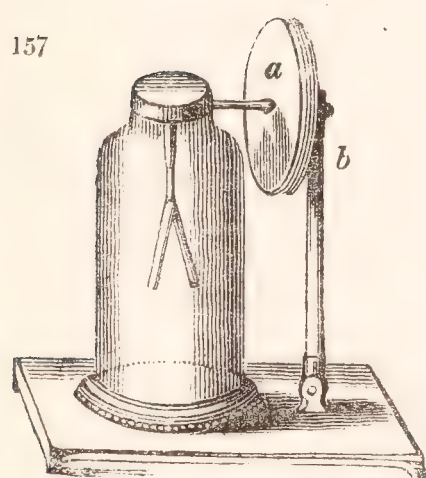
When the electrophorus is placed upon an insulating stand, its lower plate is always found in an opposite electrical state to the upper one, so that in this respect its plates resemble the coatings of a Leyden jar: it also well illustrates the great inductive capacity of the lac or resinous disc: the friction of the upper surface having communicated a polar state to the molecules which penetrates through its entire mass.

When an insulated electrified surface is opposed to another which is not insulated, so as to be affected by it by induction through the intervening stratum of air, the electricity communicated to the former suffers an increase of tension on breaking the induction by removing the opposed uninsulated conductor: this property is exhibited as follows: Provide a brass plate, five or six inches in diameter, and drop upon its lower surface three small spots of sealing-wax; place it upon a similar plate,

forming the cap of the gold-leaf electrometer, from which it will be separated about a twentieth of an inch by the three small insulated legs of wax. Connect the upper plate with the ground, by touching it, and give a very feeble electrical charge to the electrometer, so as scarcely perceptibly to diverge its leaves; then suddenly remove the upper plate, by which the induction towards it will be broken, and the tension of the electricity suddenly increased, so as to cause a very considerable divergence of the leaves.



The plates employed in this experiment have been called *condensers*. They are sometimes placed perpendicularly, as in fig. 156, and the uninsulated plate *a* is supported by a wire and joint, so as to be brought as close as possible to the insulated plate *b*, without touching; the latter is in communication with the electrometer, and having received its charge, the moveable uninsulated plate is drawn back, as in *c*, and the intensity of the electricity displayed.



Sometimes the condenser is directly attached to the electrometer, as shown in fig. 157: *a* the insulated plate; *b* the moveable plate in communication with the ground.

The general phenomena of induction already explained are well illustrated by this form of apparatus; and it will now be evident that what is termed electrical *repulsion* depends upon induction to surrounding bodies, as in the case of the gold leaves of the electrometer, or of two similarly electrified pith-balls, which cannot induce towards each other, but do so in all other directions through the molecules of the surrounding medium or dielectric. In the condenser above described, when the plates are near each other so as only to be separated by a very thin stratum of air, induction chiefly takes place from *a* to *b*; but on removing *b* to a distance, the induction of the gold leaves to the nearer surrounding objects becomes manifest, and they appear to repel each other. In these cases, more or less of the inductive force is diverted from one direction into another.

§ 10. OF NATURAL ELECTRICAL PHENOMENA.

HAVING considered electricity in relation to its most obvious and ordinary effects, we may proceed briefly to notice its influence as a *natural agent*.

Electricity is called into action, upon a grand scale, in the production of the *thunder-storm*. It has been by no means satisfactorily ascertained to what the electric accumulation, that in such cases ensues, is to be

attributed, but it is probably referable to a variety of causes, and connected with some peculiar power in masses of aërial vapor to receive and retain electrical charges, which do not admit of artificial imitation, and cannot, therefore, be satisfactorily explained by experiments upon a smaller scale.

The ancients referred the thunder-storm to the collision and attrition of clouds and vapors, impelled and agitated by currents in the higher regions of the atmosphere; and, in more modern times, before the discoveries in electricity which have been noticed, subtile inflammable and sulphureous exhalations were supposed to exist in the air, and, by their ignition and explosion, to produce the effects.

At an early period of electrical science, an analogy between the electric spark and lightning was suggested. Mr. Grey and Dr. Wall, and afterwards the Abbé Nollet, (*Leçons de Physique Expérimentale*, t. iv. p. 314, Paris, 1748,) hinted' more explicitly at this analogy. "If any one," says he, "should take upon him to prove, from a well-connected comparison of phenomena, that thunder is, in the hands of Nature, what electricity is in ours; that the wonders we now exhibit at pleasure are small imitations of those great effects which alarm us, and that the whole depends upon the same kind of mechanism; should it be shown that a cloud, formed by the action of the winds, by heat, and by a mixture of various exhalations, is, when opposite to a terrestrial object, as an electrified body when at a certain distance from one that is not electrified, I confess, such an idea, if well supported, would afford me infinite pleasure, and, that it may be supported by many plausible arguments, is obvious to any one well versed in the history of electrical phenomena. The universality of the electric matter, the rapidity of its action, its heat, and its activity in inflaming other bodies; its property of striking them externally and internally, even to their smallest parts; the remarkable instance we have of this effect in the Leyden experiment; the notion which may be legitimately adopted of the effects that might be supposed to arise from a much greater accumulation of electric power: these, and many other points of analogy which I have for some time meditated upon, almost induce me to believe that, in taking electricity as a foundation, one might form much more perfect and plausible hypotheses respecting the origin of thunder and lightning than any that have been hitherto suggested."

Such are the observations of Nollet respecting the analogies between electricity and lightning; their truth was afterwards proved by Franklin, who, like his predecessors, meditating upon the similarity of their effects, traced out further resemblances, and at length hit upon the happy expedient of sending up a common kite to an electric cloud, and thus experimentally demonstrating their identity. The following are the particulars of this curious discovery. (*Encyclop. Brit.* Art. ELECTRICITY.) He begins his account of the similarity of the electric fluid and lightning, by cautioning his readers not to be staggered at the great difference of effects in point of degree, since from that no fair argument could be drawn of the actual disparity of their nature. It is, he says, no wonder that the effects of the one should so far exceed those of the other; for if two gun-barrels electrified will strike at two inches' distance, and make a report, at how great a distance 10,000 acres of electric cloud

must strike and give its fire, and how loud must be the crash. He then adds, that flashes of lightning are generally crooked and waving, and so is a long electric spark; that lightning, like common electricity, strikes the highest and most pointed objects in its way, in preference to others, such as hills, trees, towers, spires, masts of ships, points of spears, &c.; that it takes the readiest and best conductor; that it sets fire to inflammable bodies, rends others to pieces, and melts the metals. Lightning, he adds, has often been known to strike people blind, and the same happened to a pigeon which had received a violent shock of electricity; in other cases it has killed animals, and they have also been killed by electricity.

Reasoning on these effects, and having observed that pointed conductors appear to attract electricity, he conceived that pointed rods of iron attached to buildings might draw from clouds their electric matter, without noise or danger, and dissipate it at their termination in the earth; the following is his memorandum upon this subject:—"The electric fluid is attracted by points; we do not know whether this property be in lightning, but since they agree in all particulars in which we can already compare them, it is not improbable that they agree likewise in this. *Let the experiment be made.*"

In the year 1752, while waiting for the erection of a spire in the city of Philadelphia, not imagining that a pointed rod of any moderate height would answer the purpose, it occurred to him, that by means of a common kite, he might have ready access to the higher regions of the atmosphere. Preparing, therefore, a large silk handkerchief, and two cross sticks to extend it on, he took the opportunity of the first approaching thunder-storm, and went into a field, where there was a shed proper for his purpose. But, fearing the ridicule which might attend an unsuccessful attempt, he communicated his intention to no one but his son, who assisted him in flying the kite. A considerable time elapsed without appearance of success, and a promising cloud passed over the kite with no effect, when, just as he was beginning to despair, he observed some loose threads upon the string of the kite begin to diverge and stand erect; on this, he fastened a key to the string, and on presenting his knuckle to it, was gratified by the first electric spark that had thus been drawn from the clouds; others succeeded; and when the string had become wet by the falling rain, a copious stream of electric fire passed from the conductor to his hand.

Franklin pursued these experiments with much assiduity and success; he erected an insulated iron rod to conduct the electricity of the clouds into his house, and performed with it nearly all the experiments for which he had before employed the common machine; and that no opportunity might be lost of making such experiments, he attached a chime of bells to the electric rod, which gave him notice, by their ringing, of the electric state of his apparatus.

Two French gentlemen, Messrs. Dalibard and Delor, probably were the first who experimentally verified Franklin's hypothesis. The former prepared his apparatus at Marly, near Paris; the latter at his house, which stood upon high ground in that city. Dalibard's apparatus consisted of an iron rod forty feet long, the lower end of which was brought into a sentry-box; on the outside it was fastened to three wooden

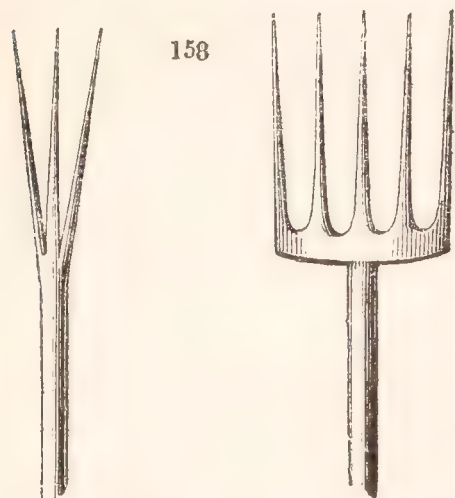
posts by silken strings defended from the rain. This machine was the first that happened to be favored by a visit from the ethereal fire. Dalibard himself was from home, but in his absence had intrusted the care of his apparatus to a person of the name of Coisier, on whose courage and attention he could depend: this person, having had all necessary instructions, was directed to call some of his neighbours, particularly the curate of the parish, whenever there should be any appearance of a thunder-storm; at length the event arrived, and on Wednesday, the 10th of May, 1752, between two and three in the afternoon, Coisier heard a loud clap of thunder; he immediately ran to the sentry-box, and, in the presence of the curate and several neighbours, drew sparks from the conductor. A few days afterwards, a successful repetition of the experiment was made by M. Delor at Paris.

These important and interesting experiments were of course repeated in almost every civilized country with variable success; in France a grand result was obtained by M. de Romas. (*Mém. de Sçavans Etrangers*, t. ii.) He had constructed a kite seven feet high, and three wide, which was raised to the height of 550 feet by a string with a fine wire interwoven through its whole length, to render it a better conductor. On the 26th of August, 1756, streams of light were darted from the string of this kite, of an inch in diameter, and ten feet long.

Considering the facility, and, at the same time, the danger of these experiments, it is curious that they have only in one instance been attended by a fatal result, namely, in the case of Professor Richman of Petersburg. He had constructed an apparatus for experiments on atmospheric electricity, which was entirely insulated, and with no contrivance for discharging it when too strongly electrified. On the 6th of August, 1753, he was examining the electricity of this apparatus in company with a friend, and whilst attending to an experiment, his head accidentally approached the insulated rod, and a flash immediately passed from it, through his body, and deprived him of life. A red spot was produced upon his forehead, his shoe was burst open, and a part of his waistcoat singed; his companion was for some time rendered senseless; the door of the room was split and torn off its hinges.

The discovery of the identity of lightning and electricity has not been without its practical results, among which we may especially enumerate the application of *Conductors* to buildings and ships, by which their safety during a thunder-storm is almost ensured. Franklin's original proposition for the purpose is that generally adopted; it consists in erecting a continuous metallic rod by the side of any building which it is intended to protect; the rod is *pointed* at each end, and extended above the highest part of the building at one extremity, the other penetrating deep into the earth, or in contact with water. In establishing this safeguard no other precautions are necessary than to have the top of the rod well and permanently pointed; and it is better of copper than iron, because the former does not so easily acquire a coating of rust, which, being a non-conductor, might possibly diminish its efficacy: it is sometimes well to subdivide the extremity into three or four points: and it should be secured to the side of the house in its descent, and penetrate so deep in the ground as always to be in free contact with a moist stratum of soil; if it ends in a deep well, so much the better. The diameter of the rod should be such as amply to

secure it against being melted by a sudden and copious flash of electricity, for which purpose half an inch is fully sufficient; and if the roof is leaded, a broad strip of lead should connect it with the conductor. When a building is very extensive, it is as well to have a conductor at each end; and where a church spire is to be protected, all clamps and bars



of metal, of any magnitude, used in its construction, should, in consequence of the danger of *lateral* explosion, have a metallic connexion, by a strip of lead or otherwise, with the nearest part of the conducting-rod. It not unfrequently happens that the iron or leaden water-pipes attached to houses act as excellent conductors, and supersede the necessity of any specific arrangement. A small building containing dangerous materials, such, for instance, as a powder-magazine, is perhaps most prudently defended

from ignition by lightning, by placing the conductor within a few yards of the building, and elevated several feet above it; for this purpose it may be attached to a mast or signal-post in the vicinity.

Conductors for ships have usually been made moveable, with the intention of occasionally attaching them to the mast during dangerous storms; the consequence has been, that they have generally remained packed up below, and not in their place at the time of danger: they are also commonly made of chain, which is improper. Mr. Harris recommends fixed conductors, and has experimentally demonstrated their safety and value.

Persons not otherwise nervous or timid, often experience particular sensations of alarm and discomfort upon the approach of a thunder-storm, arising from some constitutional peculiarity, which perhaps renders them especially sensible of the influence of electricity upon the system. These and others are often led to inquire after the best means of safety upon such an occasion; the directions to be given are few and simple. If out of doors, shelter under trees should be avoided; and if, from the rapidity with which the explosion follows the flash, it should be evident that the electric clouds are near at hand, a recumbent posture upon the ground is the most secure. It is seldom dangerous to take shelter under sheds, carts, or low buildings, or under the arch of a bridge. The distance of twenty or thirty feet from tall trees, or houses, is rather an eligible situation, for should a discharge take place, such prominent bodies are most likely to receive it, and the less elevated objects in their neighbourhood may therefore escape uninjured. It is also right, during a thunder-storm, to avoid rivers, ponds, and streams of water, for they are good conductors, and the height of a human being when connected with them is likely to determine the course of the discharge. Within doors we are tolerably secure in the middle of a large carpeted room, or when standing upon a doubled hearth-rug. We should avoid the chimney, for the iron of and about the grate, the soot that lines it, and the heated and rarefied air that it contains, may conduct the lightning; upon the same principle, gilt mouldings, bell-wires, and extensive metallic surfaces of any description, are also in danger of being struck. In bed we are comparatively safe,

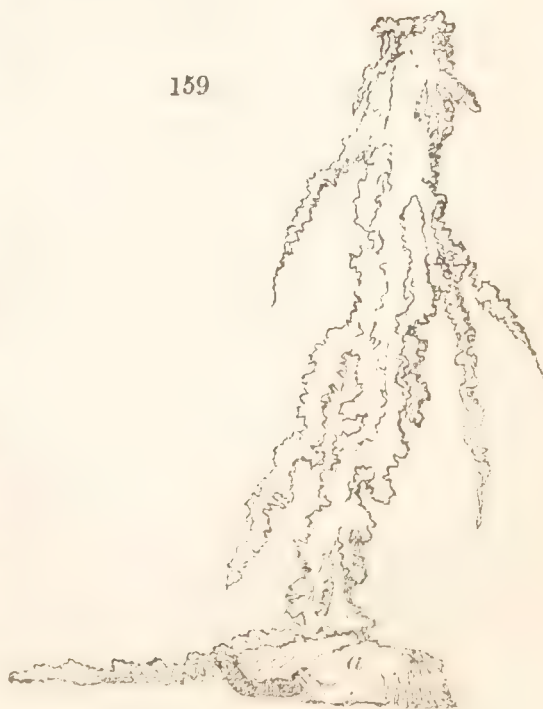
for feathers and blankets are bad conductors, and we are consequently to a certain extent *insulated* in such a situation. The cellar has been sometimes recommended as a particularly safe place of resort, and so it often is; but sometimes the basement story of a house is that which principally suffers: of this the cause is not very evident*.

We are often told that there is no danger if a certain interval of time can be counted between the flash and the report of the thunder; this is true enough; indeed, if we can count at all, we are safe. Where persons have been killed by lightning, it has generally come upon them so suddenly as to leave no time for precaution; though it must also be admitted that some have suffered from foolishly ridiculing the idea of danger, and wantonly exposing themselves to the storm, walking out to admire its grandeur, or insisting upon opening the windows to look out and observe it, or standing under a tree for shelter. A severe thunder-storm is always an awful and dangerous phenomenon; and while, on the one hand, it is the extreme of folly to neglect common precaution, or to ridicule those that are alarmed, it is, on the other, equally weak to give way to unfounded apprehension.

It is scarcely necessary here to describe a variety of amusing apparatus which has been constructed with a view to show the effects of lightning upon buildings, the means by which it harmlessly traverses good and continuous conductors, and the mischief which it produces when they are insufficient or interrupted. Models of houses, obelisks, powder-magazines, and ships, properly fitted up for these demonstrations, are sold by the philosophical instrument makers.

The appearance of the heavens during a thunder-storm, the manner in which the clouds assemble, and attract and repel each other, the circumstance of their rising against the wind, and traversing the upper regions of the atmosphere in a variety of contrary directions, are phenomena which it is not difficult to explain by reference to those general laws of electricity which have been already sufficiently explained. Upon the same principles we account for the fringed appearance of a thunder-cloud, and for the ragged excrescences which it projects towards the

* When a tree is struck by lightning, it often happens that it is completely *barked*. This arises from the electricity taking that direction which best conducts it, and which is between the bark and the wood, where there is most sap and moisture. The bark, on such occasions, is often curiously spread round the tree in the form of a circle. When lightning strikes the ground it occasionally indurates and fuses the substances through which it passes. What are termed *sand-tubes* appear to be formed by the passage of lightning through a sandy soil which it fuses in its passage. They are coated with agglutinated sand, and are about the twentieth of an inch thick, very hard, and furrowed upon the exterior. The annexed cut represents one of these tubes, as described by Mr. Irton. (*Geol. Trans.*, 1812.) In one part of its passage (at *a*) the electric fluid met with a bed of pebbles, which were fused into a mass.



earth, whilst its upper surface is generally smooth and well-defined. We sometimes observe that a number of such clouds of small dimensions coalesce into a larger one, moving swiftly in all directions, and darting flashes from one to the other, whilst the wind rises and often blows in squalls; the lightning is more frequent as the clouds aggregate, and a great expanse of the heavens often appears in an almost continuous blaze of light. The thunder, at first rumbling in the distance, now approaches with various roaring and rattling sounds, and the rain often falls in torrents.

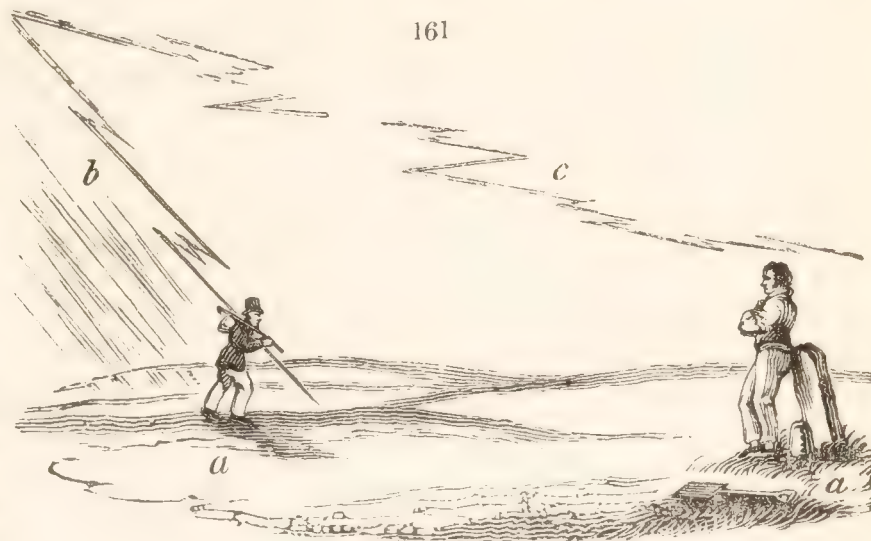
If we watch a severe thunder-storm from the beginning to the end, we observe a singular variety in the appearance of the flashes: the scene is occasionally rendered awfully magnificent by their brilliancy, frequency, and extent, darting sometimes in broad and well-defined lines from cloud to cloud, and sometimes shooting towards the earth: they are often zig-zag and irregular, and sometimes are said to appear as a large and rapidly-moving ball of fire, an appearance usually designated by the uninformed, a *thunder-bolt*, and erroneously supposed to be attended by the fall of a solid body. The report of the thunder is modified according to a variety of circumstances, depending partly upon the situation of the observer, the nature of the country, and the extent of air which it traverses. Sometimes it sounds like the firing of many muskets at a short distance off; sometimes like the clattering of loose boards upon each other, or the sudden emptying of a large cart-load of paving-stones: in these cases it usually quickly follows the lightning, and is near at hand: when more distant, it rumbles and reverberates, at first with a loud report, gradually dying away and returning at intervals, or roaring like the distant discharge of heavy artillery. In accounting for these phenomena it must be recollected, that the passage of electricity is infinitely rapid; a discharge through a circuit of many miles has been experimentally proved to be instantaneous; the motion of light is similarly rapid, and hence the flash appears momentary, however great the distance through which it passes. But with *sound* the case is very different; it is infinitely slower in its progress, moving only at the rate of about twelve miles in a minute. Now supposing the lightning to pass through a space of some miles, the explosion will be first heard from the point of the air agitated nearest to the spectator; it will gradually come from the more distant parts of the course of the electricity: and last of all will be heard from the remote extremity: and the different degrees of the agitation of



the air, and likewise the difference of the distance, will account for the different intensities of the sound, and its apparent reverberations and changes. If the observer be equidistant, or nearly so, from every part of the flash, he will hear a single crash: this will happen

if we suppose *a* (fig. 160,) to represent the observer, and *b* the direction of the flash; which is here passing in an uniform line, as it is sometimes observed to do, from a small and highly-charged cloud.

The common progress of lightning is, however, much less regular, (fig. 161,) and may be represented by the zig-zag lines *b c*, the spectators



standing at *a, a*, in which case the sound will first come to them from the nearest point, and will then seem to recede and again to approach, rumbling irregularly as the sound arrives from the different portions of traversed air, some nearer and some further from them, until it is at length lost in the distance. This irregularity in the passage of the electric discharge is sometimes so considerable, that the thunder is actually lost to the ear at one moment, and heard again at another, and this three or four times successively in the same clap.

There was at one time a controversy among electricians respecting the relative advantages of points and balls in the construction of conductors; but, consistently with Dr. Franklin's original recommendation, points are now universally adopted. Dr. Franklin suggested an experiment in proof of his opinion, which consisted in attaching to the prime conductor of the electrifying machine one or more large flocks of cotton, so as to resemble electrified clouds. When a point is made to approach these, they collapse and recede, and quickly lose their electricity: when, on the other hand, they are approached by a ball, they are attracted towards it, and the charge is more slowly dissipated.

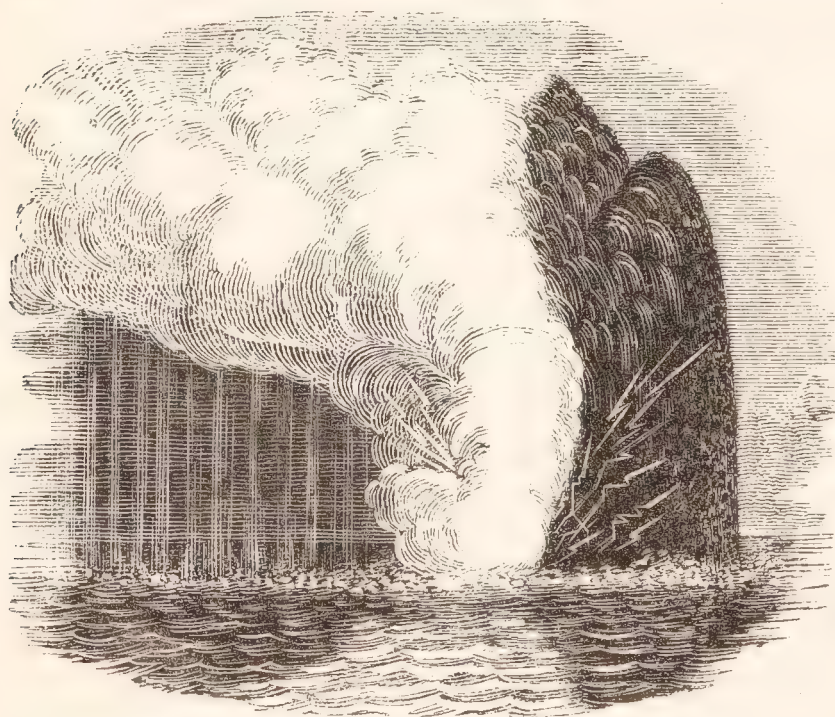
Of the cause of atmospheric electricity we are nearly ignorant: it is true that many changes which are continually going on upon the earth's surface, and in the surrounding atmosphere, are of such a nature as are known to disturb the electric equilibrium; evaporation; change of state or form in the varieties of matter; changes of temperature; chemical action; all these are sources of electrical excitation; but still they can hardly be adduced as offering a satisfactory explanation of the enormous electrical accumulation which a thunder-storm evinces. That sudden, violent, and extensive chemical and mechanical changes in the forms and states of matter are causes by which electricity is often copiously manifested, is shown by the flashes of lightning that accompany volcanic eruptions, and by the highly electric state of the surrounding atmosphere that attends them.

Another natural phenomenon, which may be referred to electric excitation, is the *waterspout*; it appears to result from the electric attraction of a mass of vapor or cloud acting upon the water beneath: it first causes the appearance of a hillock in the ocean; the water is then drawn up in a column towards the cloud, and the cloud and rain are attracted towards the water. (See in reference to the phenomena of

whirlwinds and waterspouts, LARDNER AND WALKER, *Manual of Electricity and Magnetism*, II., 241.)

It occasionally happens that volcanos suddenly break forth in the sea, and sometimes in very deep water: and they are attended by thunder, lightning, and waterspouts. Of such an eruption a curious account is given by Captain Tillard, in the *Philosophical Transactions*, and of its general appearance and effects, some notion may be formed from the following wood-cut. In June, 1811, Captain Tillard, on approaching the island of St. Michael, observed several columns of smoke rising in the horizon, which proved to issue from a marine volcano about a mile off the north-west end of the island, whither he proceeded more nearly to inspect the phenomena. "Imagine," he says, "an immense body of smoke rising from the sea, the surface of which was marked by the silver rippling of the waves, occasioned by the slight and steady breezes incidental to those climates in summer. In a quiescent state it had the appearance of a circular cloud, revolving on the water like a horizontal wheel, in various and irregular involutions, expanding itself gradually on the lee side, when suddenly a column of the blackest cinders, ashes, and stones, would shoot up in the form of a spire, rapidly succeeded by others,

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each acquiring greater velocity and breaking into various branches, resembling a group of pines; these again forming themselves into festoons of white feathery smoke. During these bursts, the most vivid flashes of lightning continually issued from the densest parts of the volcano, and the columns rolled off in large masses of fleecy clouds gradually expanding themselves before the wind in

a direction nearly horizontal, and drawing up a quantity of waterspouts, which formed a striking addition to the scene. In less than an hour a peak was visible, and in three hours from the time of our arrival, the volcano then being four hours old, a crater was formed, twenty feet high, and from four to five hundred feet diameter."

The account then goes on to state, that the eruptions were attended by a noise like the firing of cannon and of musketry intermixed, as also with shocks of earthquakes sufficient to throw down a large part of the cliff on which the observers stood; it is, however, principally to the *lightning* and to the *waterspouts* that I would here direct the reader's attention. Captain Tillard afterwards visited the volcanic island: it was eighty yards high; its crater upon the level of the sea, was full of boiling water; it was about a mile in circumference, and composed of porous cinders and masses of stone.

The *Aurora Borealis* is another natural phenomenon, probably con-

nected with or dependent upon electricity; its appearances, indeed, may be, to a certain extent, imitated by artificial electricity, which, when it passes through rarefied air, exhibits a diffused luminous stream, having much resemblance to the characteristic appearances of the northern lights. "There is," says Mr. Singer, "the same variety and intensity of color; the same undulating motions, and occasional coruscations; the streams exhibit the same diversity of character, divided at one moment into minute ramifications, and at another beaming forth in one body of light, or passing in distinct broad flashes; and when the rarefaction is considerable, various parts of the stream assume that peculiar glowing color which occasionally appears in the atmosphere, and is regarded by the uninformed observer with astonishment and fear.'

The affections of the magnetic needle and of the electrometer during the appearance of the Aurora, as well as other phenomena connected with it, have been noticed by several eminent philosophers. Halley and Dalton directed the attention of meteorologists to this subject; and, more lately, Captain Franklin has added material information upon it (*Journey to the Shores of the Polar Sea*, Appendix); it has also been accurately described by Captain Parry, who had ample opportunities of observing it in great perfection and splendor, during his perilous voyages in search of a north-west passage from the Atlantic to the Pacific. In this country the Aurora Borealis is rarely seen in perfection. On the 13th of October, 1792, it appeared in great brilliancy; and an account of it, from which the following extract is taken, has been given by Mr. Dalton in his *Meteorological Essays*. The reader may also consult the description given by Mr. Kendall of the Aurora which appeared here in October, 1829. (*Quarterly Journal of Science*.)

"Attention was first excited," says Mr. Dalton, "by a remarkably red appearance of the clouds to the south, which afforded sufficient light to read by at eight o'clock in the evening, though there was no moon nor light in the north. From half-past nine to ten there was a large, luminous, horizontal arch to the southward, and several faint concentric arches northward. It was particularly noticed, that all the arches seemed exactly bisected by the plane of the magnetic meridian. At half-past ten o'clock, streamers appeared very low in the south-east, running to and fro from west to east; they increased in number, and began to approach the zenith, apparently with an accelerated velocity; when, all on a sudden, the whole hemisphere was covered with them, and exhibited such an appearance as surpasses all description. The intensity of the light, the prodigious number and volatility of the beams, the grand intermixture of all the prismatic colors in their utmost splendor, variegating the glowing canopy with the most luxuriant and enchanting scenery, afforded an awful, but, at the same time the most pleasing and sublime spectacle in nature. Every one gazed with astonishment; but the uncommon grandeur of the scene only lasted about one minute; the variety of colors disappeared, and the beams lost their lateral motion, and were converted into the flashing radiations. Notwithstanding the suddenness of the effulgence at the breaking out of the Aurora, there was a remarkable regularity in the manner; apparently a ball of fire ran along from east to west with a velocity so great as to be barely distinguishable from one continued train, which kindled up the several rows

of beams one after another; these rows were situate before each other with the exactest order, so that the bases of each row formed a circle crossing the magnetic meridian at right angles: and the several circles rose one above another, so that those near the zenith appeared more distant from each other than those near the horizon, a certain indication that the real distances of the rows were nearly the same." This Aurora continued for several hours; there were many meteors, or falling stars, seen at the same time, but they appeared to be below, and unconnected with the Aurora.

During Captain Parry's voyage, he had numerous opportunities of witnessing the Aurora in uncommon magnificence. The following is an abstract of his description of its appearance on the 14th of December, 1821. (*Second Voyage for the Discovery of a North-West Passage*, p. 142.) "The Aurora began to show itself as soon as it was dark. Innumerable streams of white and yellowish light occupied the heavens to the southward of the zenith, being much brighter in the south-east, from whence it often seemed to emanate. Some of these streams were in right lines, others crooked, and waving in all sorts of irregular figures, moving with inconceivable rapidity in various directions. Among them might frequently be observed shorter bundles of rays, which, moving even with greater velocity than the rest, have acquired the name of 'merry dancers.' In a short time the Aurora extended itself over the zenith about half way down to the northern horizon, but no further, as if there was something in that quarter of the heavens which it did not dare to approach. About this time, however, some long streamers shot up from the horizon in the north-west, which soon disappeared. While the light extended over part of the northern heavens, there were a number of rays assuming a circular or radiated form near the zenith, and appearing to have a common centre near that point, from which they all diverged. The light of which these were composed appeared to have inconceivably rapid motion in itself, though the form it assumed, and the station it occupied in the heavens, underwent little or no change for perhaps a minute or more. This effect is a common one with the Aurora, and puts one in mind, as far as its motion alone is concerned, of a person holding a long ribbon by one end, and giving it an undulatory motion through its whole length, though its general position remains the same. When the streams or bands were crooked, the convolutions took place indifferently in all directions. The Aurora did not continue long to the north of the zenith, but remained as high as that point for more than an hour; after which, on the moon rising, it became more and more faint, and at half-past eleven was no longer visible.

"The color of the light was most frequently yellowish-white, sometimes greenish, and once or twice a lilac-tinge was remarked, when several strata appeared as it were to overlay each other by very rapidly meeting, in which case the light was always increased in intensity. The electrometer was tried several times, and two compasses exposed upon the ice during the continuance of this Aurora, but neither was perceptibly affected by it. We listened attentively for any noise which might accompany it, but could hear none, but it was too cold to keep the ears uncovered very long at one time. The intensity of the light was something greater than that of the moon in her quarters. Of its dimming the

stars there cannot be a doubt. We remarked it to be in this respect like drawing a gauze veil over the heavens in that part, the veil being most thick when two of the luminous sheets met and overlapped. The phenomenon had all the appearance of being full as near as many of the clouds commonly seen, but there were none of the latter to compare them with at the time."

My object in the above extracts has been to give an account of those appearances of the Aurora which seem to connect them with electricity, and though Captain Parry neither observed the electrometer nor the magnetic needle to be influenced, Captain Franklin (*Journey to the Shores of the Polar Sea*, App.) remarked them both to be affected. Nairne, Cavallo, and others, have described a peculiar hissing noise as one of the accompaniments of the Aurora; and Dr. Halley, in his description of a remarkable Aurora, (*Phil. Trans.*, vol. xxx.) ascribes its production to the same influence as that which produces magnetism; and Beccaria conceived the phenomena of magnetism to be dependent upon a circulation of the electric fluid from north to south, originating from several sources in the northern hemisphere.

All *meteors* were at one time considered as derived from electricity; but the showers of stones by which many of them are accompanied show that they must often be ascribed to other sources. What are termed *falling stars* are supposed by some to be of electric origin. These vary a little in size and color, moving in various directions, but chiefly appearing to shoot towards the earth. They are most common in those states of the atmosphere favorable to electric accumulation, especially on clear frosty nights, or when the sky is cloudless and the wind easterly; in the clear intervals of a showery evening, and on summer nights, when well-defined clouds are floating in a serene atmosphere. They are also common during the prevalence of the Northern Lights, appearing then to be lower than the Aurora; and from their comparative brilliancy, probably moving through a more dense medium.

The appearance of a shooting star may be imitated by discharging a Leyden jar through an imperfectly-exhausted glass tube, or air-pump receiver. The tube should be capped with brass at both ends, and about three feet long and an inch in diameter; if too perfectly exhausted the spark passes in a divided and pale stream of light, but on admitting a little more air it traverses in the form of a bright flash or spark.

It appears from the best-conducted experiments on atmospheric electricity, that in the usual state of the atmosphere it is generally *positive*, but that it frequently changes to *negative* upon the first appearance of rain, snow, or hail. The approach of clouds often influences the electricity of the conductor, so as to produce alternations of the two electricities. There appears, as might be expected, to be a greater accumulation of electricity in the atmosphere during the presence of regular thunder-clouds, than at any other period; a driving fog, accompanied by small rain, a fall of snow, and a smart shower on a hot day, are also attended by powerful signs of electric excitation. Hot weather succeeding wet, or wet weather following a series of dry days, are also favorable circumstances for the generation of atmospheric electricity. The atmosphere is least electrical during the prevalence of north-easterly winds, and in that state which produces a disagreeable sensation of dryness and of cold

without a corresponding depression of the thermometer. It has also been remarked, that the usual positive electricity is weakest during the night; that it increases with the sun-rise; decreases toward the middle of the day, and again increases as the sun declines; it then again diminishes and remains feeble during the night; it would, therefore, seem probable that the electricity of the atmosphere is influenced by the same causes that modify the distribution of moisture. A valuable epitome of the phenomena of atmospheric electricity, by Mr. Charles V. Walker, will be found in the second volume of his *Manual of Electricity, &c.* The reader is also referred upon this and other parts of electric science, to the *Transactions of the Electrical Society.*

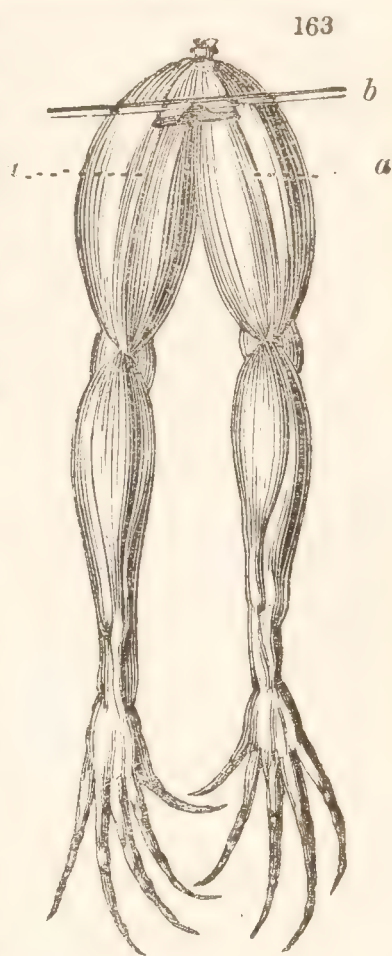
§ 11. GALVANISM AND VOLTAIC ELECTRICITY.

WE have now acquired such preliminary information upon the subject of electrical excitation, and of the phenomena exhibited by electrified bodies in general, as may enable us to proceed to other cases of the evolution of this singular agent. We may observe, that scarcely any change in the general state of matter is unattended by more or less disturbance of the electrical equilibrium. Thus the disruption of solid bodies, changes of temperature, changes of form, are sources of electricity; breaking up a mass of sugar, tearing asunder the plates of mica, cleaving a piece of dry wood, heating certain minerals, evaporating liquids, and condensing vapors, may be cited as instances, which have been or will be noticed. But among the changes in the conditions of matter which are attended by the evolution of electricity, those resulting from or connected with chemical action are apparently the most important, and are immediately connected with those curious cases of the manifestation of electricity, commonly described under the terms *galvanism* and *voltaic electricity*.

In the year 1790, Galvani, of Bologna, discovered that electric sparks taken in the vicinity of a recently killed frog, produced spasms of the muscles: and it was soon after found if the sciatic nerve of a frog be laid bare, and touched with a piece of *zinc*, whilst, at the same time, the muscle is touched with *gold*, similar effects to those of the electricity were produced whenever the metals were brought into *contact*, or connected together by *conductors*. If non-conductors were used to connect the metals, no spasm ensued. Cold-blooded animals retain this kind of excitability longer after death than others, and they are affected by states of electricity so feeble as not to be indicated by the most delicate electrometers. A feeble spark, or the most trivial charge of a Leyden phial, produces analogous effects. These facts soon attracted considerable attention, and were followed up with much diligence and singularly extensive and important results*.

* "It would be difficult in the history of science to find a more signal example of the influence of circumstances apparently fortuitous, on the progress of discovery, than that furnished by the invention of the Voltaic pile. 'It may be proved,' says Arago, 'that this immortal discovery arose in the most immediate and direct manner from a slight cold with which a Bolognese lady was attacked, and for which her physician prescribed the use of frog broth.'" (LARDNER.)

Frogs are the most convenient and susceptible animals for these experiments; but when they cannot easily be obtained others may be substituted. The annexed sketch (fig. 163) represents the legs of the frog prepared for galvanic experiments: the skin is removed, and the crural nerves *a a* are then easily found, by gently separating the muscles: *b* is a silver wire passed under both the nerves for the convenience of ensuring metallic contact: if the legs be now folded up and placed upon a plate of zinc, convulsions are produced whenever a metallic communication is made between the wire *b* and the zinc plate. A similar experiment may be made with a live flounder, which may generally be procured at the fishmonger's. Place the flounder in a plate upon a slip of zinc, and put a shilling upon its back; then, with a piece of wire connected with the zinc, make occasional contacts upon the shilling, and at each contact strong muscular contractions are produced. According to Dr. Ure, (*Dictionary*, Art. GALVANISM), the degree of muscular contraction depends upon the direction of the electric current, and is greater when the zinc touches the nerve, and the copper or silver the muscle, than when this order is reversed*.



In these experiments, if the separate pieces of metal be of the *same* kind, no effects are observed: to produce them, two *different* metals are requisite, and these must be in contact; and those metals which are difficultly acted upon by acids, opposed to those which are easily acted on, form, in general, the most powerful combination. Thus, gold and platinum produce scarcely any effect; but gold, or platinum, or silver, opposed to iron, tin, or zinc, are effectual. This part of the subject will, however, be more explicitly inquired into afterwards.

There are many other experiments and illustrations relating to this subject, two or three of which may be here noticed. If a piece of silver be placed *upon* the tongue and a piece of zinc *under* it, no effect is observed, whilst the metals are kept apart; but, if their ends be brought into contact, we immediately perceive a saline taste, and a peculiar sensation, somewhat resembling a slight electrical shock; sometimes, also, when the surface of the metals is extensive, a flash of light appears to pass before the eyes. This latter effect may be more certainly produced

* The phenomena mentioned in the text have given rise to various experiments in reference to the relation between electricity and the vital functions; among these researches, those contained in Dr. Wilson Philip's communications to the Royal Society, and in his *Experimental Inquiry into the Laws of the Vital Functions*, are the most precise. Attempts have also been

made to apply the stimulus of electricity in cases of suspended animation, from suffocation and drowning. Dr. Ure's account of the effects of galvanism upon the body of a criminal executed at Glasgow, deserves the attentive perusal of those who are concerned in these medical and physiological applications of electricity; but the subject is too extensive to be entered upon here in detail.

by placing one metal between the upper lip and the gums, and the other upon the tongue, and bringing their ends together as before.

To account for these, and similar effects, it was by some supposed that the nerves and muscles of animals were in opposite electrical states, and that the spasms were produced in consequence of their annihilation by the metallic conductor. But this hypothesis was controverted by Volta, who showed that contractions might be excited by the application of two different metals, but not by one only, and referred the effect to the *electromotive power of the different metals*.

When two dissimilar metals were brought into contact, he found that very feeble electrical states were developed in them. When an insulated plate of zinc was brought into contact with one of silver or copper, the former was found to be in a feebly *positive* state, and the latter *negative*, as if a minute portion of electricity had passed *from* the least *to* the most oxidable metal. To this supposed transfer, or disturbance of electricity, Volta referred the convulsive motion of the frog's limbs, considering the nervous irritability of the animal as highly susceptible of such influence, and as operating as an extremely sensible electroscope; and the production of similar convulsive twitches by common electric sparks and shocks, was adduced in favor of this opinion.

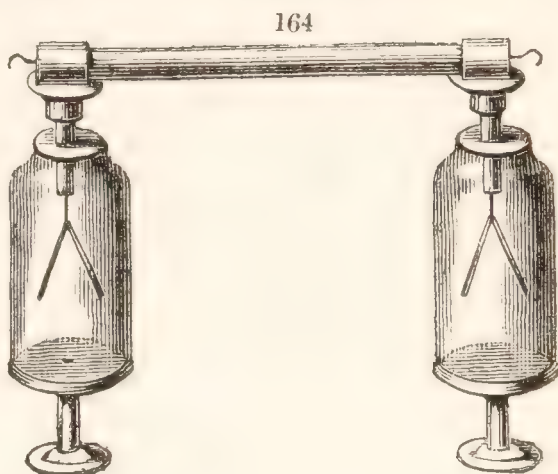
The following experiment has also been referred to, as a case of electrical excitation, depending upon the *contact* of dissimilar metals: Place a large plate of metal upon the cap of the gold-leaf electrometer, and sift *zinc* filings upon it through a *copper* sieve, held by a glass handle: the leaves will diverge with *positive* electricity, and the sieve will acquire a *negative* state. Repeat the experiment, substituting a *zinc* sieve and *copper* filings, for the copper sieve and zinc filings, and the divergence of the electrometer will be *negative*, the sieve being *positive*. But when we recollect by what slight causes electricity is sometimes made evident, it becomes a question whether mere *contact* is the only source of its development in these and the preceding cases; whether friction, change of temperature, or even, ultimately, chemical action, may not interfere.

Although we shall find that, in reference to the source of what has been termed voltaic electricity, mere *contact* is an element of very doubtful importance, I shall here proceed to describe an instrument which has been supposed to illustrate this mode of electrical excitation: it will serve on the one hand to connect them with the preceding details of the phenomena of frictional electricity, and on the other with those of chemical origin. It is termed, from its inventor, *De Luc's electric column*. It consists of a number of alternations of two metals, with interposed paper; for this purpose thin paper covered with *gold* or *silver* leaf may be used, punched out into circular discs of about half an inch diameter, and alternating with similar discs of thin *zinc* foil, so arranged that the same order of succession, namely, zinc, silver, paper: zinc, silver, paper, &c., may be kept up throughout. About five hundred such alternations will be required to produce an active column, and they are most conveniently placed in a suitable glass tube, perfectly clean and dry within, and surmounted at each end with a brass cap, perforated by a screw, by which the plates may be pressed together and which also serve as the poles of

the arrangement; the screw at one end being in contact with the zinc plate, and that at the other with the silvered paper*.

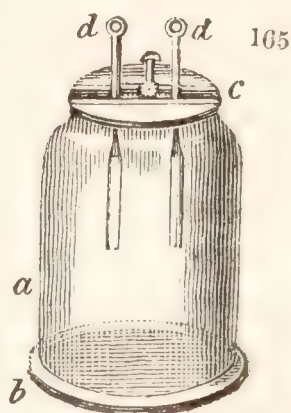
If we hold this column by one of its brass caps, and with the other touch the cap of the gold-leaf electrometer, a divergence will be communicated to the leaves, which will be found to be *positive* from one end, and *negative* from the other of the arrangement.

If we place the column with each of its extremities in connection with the electrometers, as represented in the annexed cut (fig. 164), and if we suppose the arrangement of the discs such as to commence on the left hand with a silver plate, and to terminate on right with a zinc plate, the alternation being silver, zinc, paper,—silver, zinc, paper, (SZ. P. SZ., &c.) then, the instrument on the right in connection with the terminal zinc plate will be *positively* diverged, and that on the left in connection with the initial silver plate, will be *negatively* diverged; and on making a direct communication between the two electrometers by a metallic wire, the divergence ceases, but again ensues soon after such communication is broken. It will generally be found most convenient in experiments with the column to employ two, each containing about 500 discs; these may be united end to end, so as to form one continuous arrangement.



If then, we examine into the state of the electricity thus excited, we find it resembling that of a conductor under induction: there is a positive and a negative end, and a central point, which is neutral; upon making a communication between either end of the column and the ground, the electricity of the opposite end becomes proportionally exalted.

In the experiments we are now about to describe, it will be found convenient to employ an electroscope in which each gold leaf is separately insulated, and so arranged as to admit of their being brought nearer to, or carried further from each other. Such an instrument is represented in fig. 165, where *a* is a glass cylinder mounted upon a brass or wooden base, *b*; the cover, *c*, is a thin piece of dry and varnished wood, with a slit in it, in which the glass tubes, *dd*, slide backwards and forwards, and through which, brass wires pass, with a slip of gold leaf attached to each of their lower extremities.



If we now, having duly adjusted the distance between the gold leaves, bring the *zinc* ends of the columns in contact with each of the wires to which they are attached, the leaves *repel* each other; the *silver* ends produce a similar effect: but, if one of the gold leaves be connected with the *zinc* end, and the other with the *silver* end of the column, they

* Analogous arrangements were made by Hachette and Desormes, with pairs of metallic plates, separated by layers of paste mixed with salt; and by Zamboni, who

used discs of paper, gilt or silvered on one side, and covered on the other with a mixture of black oxide of manganese and honey.

attract each other; and having thus, by contact, annihilated their opposite electrical states, they separate for a moment, and then again attract and separate as before, a kind of perpetual motion being kept up between the leaves in consequence of the successive electrical charges communicated to them by the column. Upon this principle a variety of instruments have been constructed, under the name of *perpetual motions*: thus, a small clapper may be kept constantly vibrating between two bells; or a light pendulum between two conducting surfaces; and these motions may be made to continue as long as the column retains its electric activity, which is often for months or years.

If one end of De Luc's columns be connected with the *interior*, and the other with the *exterior* of a Leyden jar, the jar will receive a charge; its knob will affect a gold-leaf electrometer, and on discharging it by a wire, a very small spark will be observed. To obtain this spark, or any luminous appearance, without the intervention of the jar, requires a very extensive series of the metallic alternations.

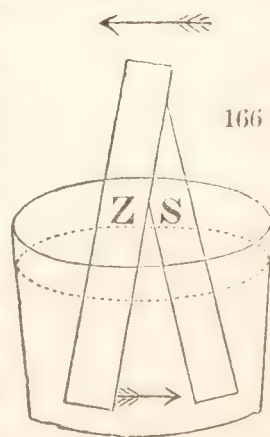
It will be observed, in regard to this instrument, that its electrical excitement is chiefly that of intensity, and that after its discharge a sensible time intervenes before its power is renewed: its electricity is *apparently* independent of chemical action, and has therefore been considered referable only to the *contact* of the metals. In favor of this opinion it has been urged that whenever any chemical action is apparent in it, its electrical effects cease, as when the zinc or silver becomes tarnished, or the intervening papers more than ordinarily damp; but it is also rendered inactive by perfectly drying the papers so as to deprive them of their hygrometric moisture; and it is said that in the course of years the zinc becomes evidently corroded. It was always presumed that no chemico-electrical effects could be obtained from these piles, but Mr. Gassiot has succeeded in decomposing iodide of potassium by a column of 10,000 series upon Zamboni's construction. (*Phil. Trans.*, 1839, p. 191.) As regards the general phenomena of these arrangements, we shall find that they closely correspond with those of what has been termed the *water-battery*; namely, a very extensive voltaic series of zinc and silver, or zinc and copper, charged with common water; and in reference to the independence of the source of electricity upon chemical action, it may be remarked, that if all possible sources of such action be excluded, the instrument becomes inactive.

In reference to the cases of electrical excitation by the contact of different metals immersed in very dilute acids, it is found that the most oxidizable metal is always *positive*, in relation to the least oxidizable metal, which is *negative*, and the more opposite the metals in these respects, the greater the electrical effect; and if the metals be placed in the following order, each will, when immersed in water, or in extremely dilute sulphuric acid, become *positive* in relation to that which precedes it, and *negative*, to that which follows it; and the greatest effect will result from the contact of the most distant metals. Platinum—Gold—Silver—Mercury—Copper—Tin—Lead—Iron—Zinc—Sodium—Potassium. Here we have presumptive evidence in favor of a chemical cause as the source of electricity, for it is not produced by the most dissimilar *conductors* either of heat or of electricity, but by those which are most opposed in the facility with which they are acted upon by oxidizing agents; and it will be moreover found that, upon this *chemical action*, the

direction of the current entirely depends. So that, for instance, if copper in contact with iron be placed in dilute sulphuric acid, the oxidizing agency of such aqueous acid will be limited to the iron, and the electric current will be from the iron to the copper; but if we substitute a solution of sulphuret of potassium for that of sulphuric acid, the chemical action will then be greatest upon the copper, and the direction of the electric current will be reversed. It will be obvious, therefore, that all tables of the electric powers of the metals must be constructed in reference to the exciting fluid selected, upon which the direction of the current essentially depends, and not only do different liquids produce in this respect different effects, but the same fluid in different states of dilution, exerting as it often does different chemical effects upon the same metal, will give rise to corresponding modifications of the electric current. The following table, from "FARADAY'S Experimental Researches," (17th series, *Phil. Trans.*, 1840,) well illustrates these points. The metals are numbered in the order which they presented in dilute nitric acid, for the purpose of showing by the comparison of those numbers in the other columns the striking departures there from this the most generally assumed order. Each metal is positive to that which *precedes* it, and negative to that which follows it, the negative being in all cases above.*

Dilute Nitric Acid.	Dilute Sulphuric Acid.	Hydrochloric Acid.	Strong Nitric Acid.	Solution of Caustic Potassa.	Colorless Bi-hydrosulphuret of Potassium.	Yellow Hydrosulphuret of Potassium.
1 Silver	1 Silver	3 Antimony	5 Nickel	1 Silver	6 Iron	6 Iron
2 Copper	2 Copper	1 Silver	1 Silver	5 Nickel	5 Nickel	5 Nickel
3 Antimony	3 Antimony	5 Nickel	3 Antimony	2 Copper	4 Bismuth	4 Bismuth
4 Bismuth	4 Bismuth	4 Bismuth	2 Copper	6 Iron	8 Lead	3 Antimony
5 Nickel	5 Nickel	2 Copper	4 Bismuth	4 Bismuth	1 Silver	8 Lead
6 Iron	6 Iron	6 Iron	6 Iron	8 Lead	3 Antimony	1 Silver
7 Tin	8 Lead	8 Lead	7 Tin	3 Antimony	7 Tin	7 Tin
8 Lead	7 Tin	7 Tin	8 Lead	9 Cadmium	2 Copper	9 Cadmium
9 Cadmium	9 Cadmium	9 Cadmium	10 Zinc	7 Tin	10 Zinc	2 Copper
10 Zinc	10 Zinc	10 Zinc	9 Cadmium	10 Zinc	9 Cadmium	10 Zinc

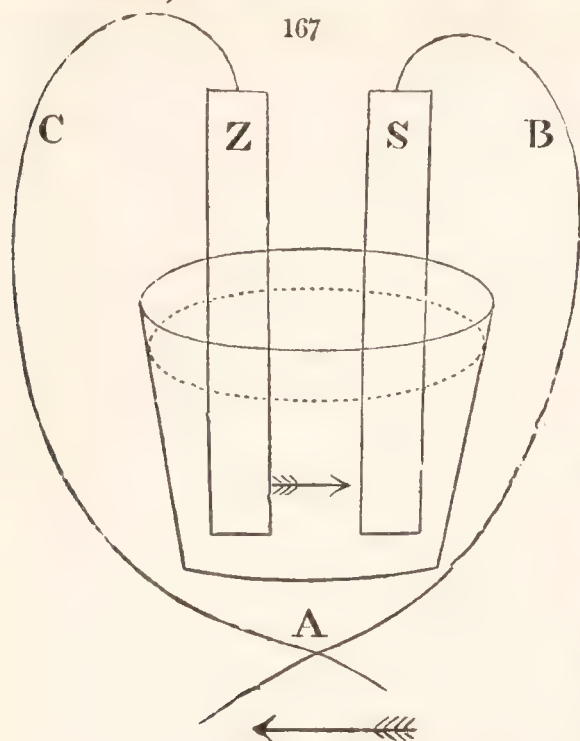
We may now proceed to the further examination of the phenomena arising out of the evolution of electricity by chemical agencies. What is commonly called "a simple galvanic or voltaic circle," is formed by immersing *two different metals in a dilute acid*, and making a communication between them, either by direct contact, or by some perfect conductor; one of the metals should be easily, and the other difficultly, or not at all, acted upon by the liquid, and the more opposite the metals are in these respects, the more powerful are the electrical effects observed. In fig. 166, z represents a plate of zinc, and s one of silver, partly immersed in very dilute sulphuric acid, and in contact at their upper ends; by such arrangement a current of electricity is established, passing from the zinc through the liquid to the silver, and from the silver again to the zinc, in the direction of the darts. Or the arrangement may be modified, by immersing the plates separately in the acid, and connecting them by wires, as in fig. 167: the circuit will thus be



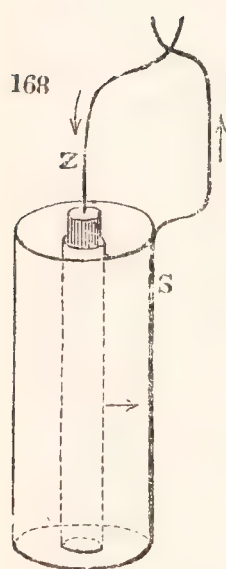
* It will be observed that in this table, tin, in column 2 and 3, stands below iron, and therefore electro-positive to it; but this depends upon the strength of the acid, which in column 2 was in the proportion of one

measure of strong acid to thirteen of water, and in column 3 in that of equal measures; in a much weaker acid iron is electro-positive to tin, as also in common water.

extended, but the electrical current will be found moving in the same

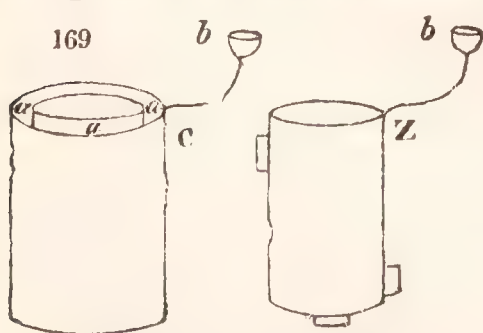


direction, from the zinc across the liquid to the silver, and through the wires from the silver to the zinc, in the direction represented by the arrows. In thus completing the circuit by wires, the electric current may conveniently be transferred through fluid and other bodies, and the circuit may be broken and restored at pleasure, by alternately separating and renewing the contact of the wires at A. It will be observed, that in consequence of the direction of the electric current in this arrangement, the wire B, connected with the silver plate, is conveying electricity to the wire C, united to the zinc plate.



This arrangement may be modified by interposing a few folds of blotting paper, or a piece of flannel dipped in the acid, between the plates, instead of immersing them into the acid itself; or, as in the annexed sectional diagram (fig. 168), the silver or copper plate may itself be formed into a vessel for containing the acid, s representing the wire connected with the vessel, and z a wire connected with the zinc plate, care being taken that the plate is nowhere in *metallic* contact with the cup.

Another useful modification of this form of apparatus is the following: c is a cup, composed of two cylinders of sheet copper, placed one within the other, and closed at bottom, to contain dilute acid: z is a zinc cylinder with a few pieces of cork attached to it, so as to prevent its touching the sides of the cup a, when introduced into its place between them: bb are small copper cups, soldered to conducting wires, and containing a little mercury, for the purpose of conveniently making and breaking the circuit.



To understand many of the peculiar phenomena presented by these and similar arrangements, it will be necessary to refer to the important distinctions between electricity of *tension*, accumulated upon surfaces, and manifesting itself by attractions and repulsions, and by discharges passing through air; and electricity in *motion*; the *intensity* of the electricity produced by these simple circles is either null, or so trifling as to require extremely delicate means to render it sensible; but its *quantity* is great; and, accordingly, if we make it traverse a fine metallic wire, placed between the wires A, fig. 167, or z and s, fig. 168, or between the cups bb, fig. 169, the wire will become hot, and often ignited; a spark will pass between two fine charcoal points when brought into contact, and then removed from each other; the *galvanometer* will be powerfully deflected; and certain compound substances, made part of the circuit, will be

decomposed : here, then, we have, as evidences of the *current* of electricity above alluded to, the production of heat and light, and of magnetic and chemical effects.

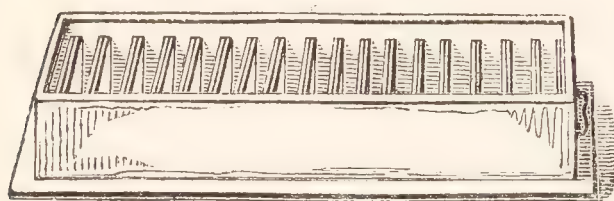
There are two circumstances which materially interfere with the *quantity* of electricity put into motion by these arrangements. The one is the *size of the plates*, and the other the *nature and strength of the interposed acid or liquid*; or, in other words, the nature and energy of the *chemical action*. By increasing the superficial extent of the plates, the extent of the chemical action of the intervening fluid is increased, and the *quantity* of electricity proportionately augmented; and in the case of zinc and dilute sulphuric acid, the more rapidly the zinc is oxidized, and the oxide removed, so as to expose successive new surfaces to the agency of the intervening fluid, the greater is the quantity of electricity which traverses the circuit. Indeed, the heating effects of a single pair of plates of great extent of surface is such, that instruments so constructed have been termed *calorimotors*. In an arrangement for this purpose, made under the direction of Mr. Pepys, at the London Institution, (*Phil. Trans.*, 1823,) a sheet of zinc and one of copper were coiled round each other, each being 60 feet long and 2 wide; they were kept asunder by the intervention of hair-ropes, and suspended over a tub of acid, so that by a pulley they could be immersed and removed.

In all these cases, however, the *intensity* of the electricity remains the same, or nearly the same, and, to increase it, we resort to increase of the *number* of the alternations of metals and acid; this constitutes “a compound galvanic circle,” and leads to the arrangement originally devised by Volta, and hence termed the *VOLTAIC pile* or *apparatus*. Volta’s original pile consisted of a number of plates of two different metals, alternating with moistened flannel or pasteboard, and arranged in regular order of succession. Zinc and copper are the metals commonly used; zinc and silver, or zinc and platinum, furnish a more active series, but the use of the latter metals, in extensive combinations of this description, is to a great extent prohibited by their expense.

To construct the *voltaic pile*, take from twenty to fifty plates of copper, and as many of zinc, from two to four inches square, and pile them in a glass dish, or upon a plate, in regular order, with an intervening piece of flannel of the same size, well soaked in a solution of common salt in water, taking care that the regular succession of metals and saline solution is kept up through the series, in such an order that if we begin with a plate of zinc, upon it will be a piece of the moistened flannel; then a copper plate, a zinc plate, and a piece of flannel; then copper, zinc, flannel, and so on; the series terminating with a copper plate. Having made this arrangement, connect a wire by *perfect metallic contact* with the lowest, or zinc, and a similar wire with the uppermost, or copper plate, having previously slipped a small piece of glass tube upon the wires, to serve as an insulating handle; then, on bringing the upper wire from the terminal copper plate, into contact with the condensing electrometer, it will diverge the leaves *positively*, and the lower wire from the bottom zinc plate *negatively*, and the same general phenomena will be observed as in De Luc’s column. If the fingers be thoroughly moistened by rubbing them with salt and water, so as in some measure to overcome the non-conducting power of the cuticle, a slight shock will be per-

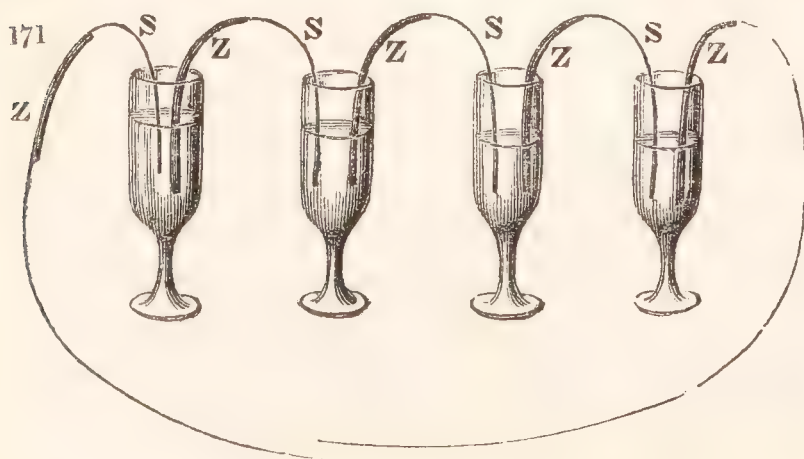
ceived on touching the extreme wires with each hand : a spark is rarely observed, even in a dark room. But if we now substitute dilute nitro-sulphuric or nitrohydrochloric acid, for moistening the intermediate flannel, we may not perhaps observe any material change in the power of the pile, as indicated by the affections of the electrometer : but the shock will probably be a little more powerful ; and a *spark* will be perceived, on bringing the poles together, more especially brilliant when taken between two points of well-burned charcoal attached to the wires from the top and bottom of the pile. Also, if we now bring the wires from the extremes of the pile (which for this purpose should terminate in strips of platinum) near each other, in a glass of acidulated water, gas will be extricated at each conductor. In this apparatus, arranged as just described, the direction of the electric current when the circuit is completed, is from the zinc plates, through the saline or acid solution, to the copper plates ; so that the inferior zinc plate forms what has been termed the *negative*, and the superior copper plate, the *positive* end or pole of the series.

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In the construction of the Voltaic pile, as just described, much inconvenience results from the method of arrangement, when the plates are numerous ; and the weight of the upper part of the pile presses the moisture out of the lower part, and renders it comparatively inactive. To obviate this, each pair of plates is sometimes soldered together, and cemented in regular order, into a well-seasoned mahogany trough, as in fig. 170 ; and the intervening cells, which are about a fourth of an inch wide, are filled with acidulated water, or other proper liquid, by which the arrangement is rendered active. The apparatus thus constructed was called a *voltaic trough*, and the combination of several of them, a *voltaic battery* ; such troughs are easily filled and emptied, and may be kept clean by rinsing out with water, after use. A wire, in metallic contact with each terminal plate, enables us, as before, to complete the circuit.

Another form of Volta's apparatus, the "*Couronne des tasses*," consists in arranging a row of small glasses or cups, (figs. 171, 172,) containing dilute sulphuric acid (or other proper liquid), in each of

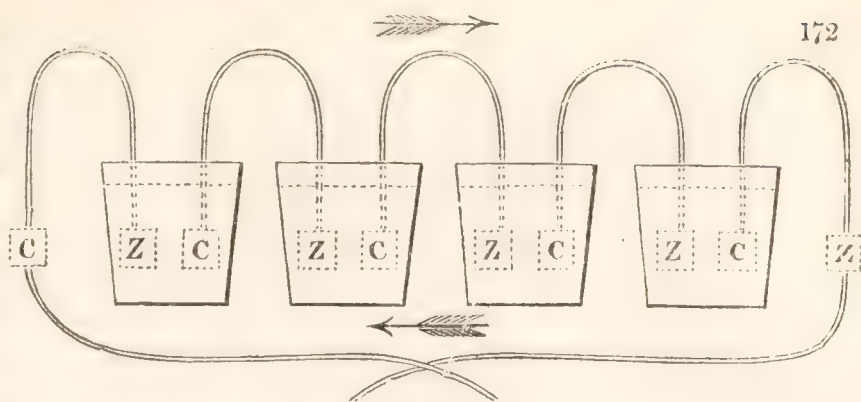


which is placed a plate or wire of platinum, silver, or copper, and one of zinc, not touching each other, but so connected, that the zinc of the first glass may be in metallic contact or communication

with the silver or copper of the second, and the zinc of the second glass with the silver or copper of the third, and so on throughout the series, as shown in the annexed cuts.

By arrangements of this kind, we can see what happens in each cell of the apparatus ; and it will be observed, that when the extreme wires or

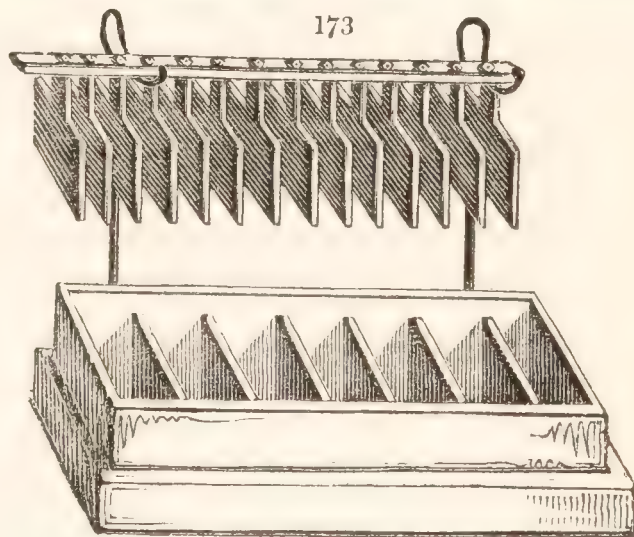
poles are *in contact*, and a current of electricity therefore passing through the arrangement in the direction of the arrows, each wire or metallic surface immersed in the liquid is active; whereas,



when the connexion between the poles is broken, the silver (or the copper) cease to evolve gas. In other respects, the general properties of the apparatus thus arranged, resemble those of the other forms above described.

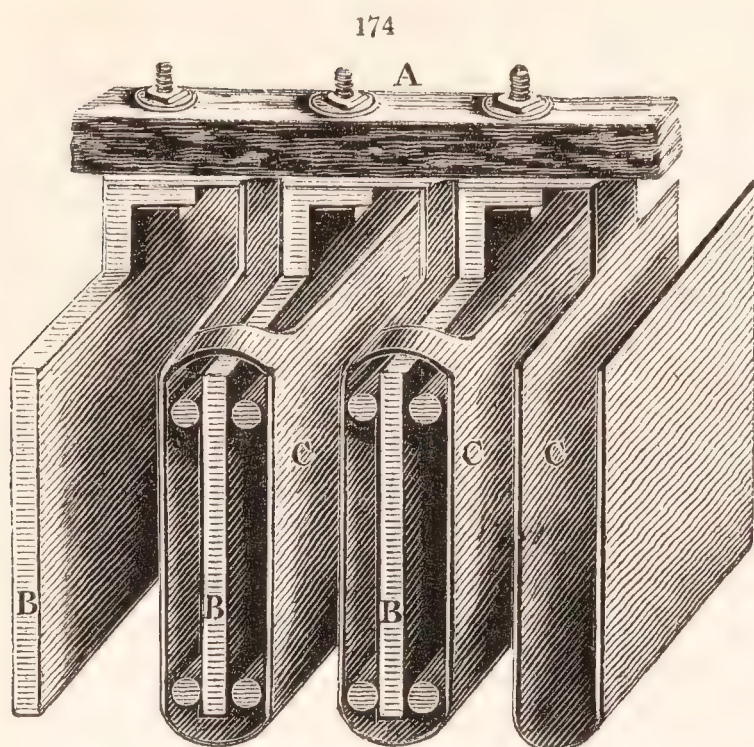
Another good form of the voltaic apparatus is constructed upon similar principles: it consists of a trough of earthenware, with partitions of the same material (fig. 173). The plates of copper and zinc are soldered together at one point only, and each united pair of plates is so arranged, as to inclose a partition between them; consequently, there is in each cell, a copper plate connected with the zinc of an adjoining cell, and so on, in regular succession; and the connecting piece of the last copper plate may be elongated, so as to enable it to dip into the first cell of the next trough, when several of such troughs are placed in rows endways to each other; it is there opposed to the ensuing zinc plate of another set, and so on.

The plates are attached to a slip of baked wood, so that the whole may at once be lifted into or out of the cells. This construction, originally suggested by Dr. Babington, has many advantages; it admits the fluid to remain in the trough, while the action of the plates may be suspended at pleasure, by lifting them from the cells; when the plates are corroded or injured, they are also easily replaced. Where many of



these troughs are employed, so as to constitute a powerful battery, it is necessary to be extremely attentive to the regular order of succession throughout the series; if any plates are misplaced, or any single set reversed, a great diminution of effect is the consequence. Much care must also be taken respecting the communications between the troughs to prevent the accidental displacement of any of the junction-plates. It is well to be provided with a few spare pairs of plates attached to each other by a sufficiently long copper strap, for the purpose of uniting the troughs, where their arrangement requires that they should be placed at angles to each other.

A considerable improvement in the construction of this apparatus was suggested in the year 1815 by Dr. Wollaston. It consists in extending the copper plate, so as to oppose it to both surfaces of the zinc, as shown in the following sketch (fig. 174), where A represents the bar of wood to which the plates are screwed; BB the zinc plates connected as usual with the copper plates c c, which are doubled over the zinc plates, and



opposed to them upon all sides, contact of the surfaces being prevented by pieces of wood or cork placed between them, which keep the plates about one-fourth of an inch asunder.

There are many inconveniences, however, attending each of these forms of the Voltaic apparatus, and many important points respecting its phenomena, which cannot be conveniently investigated by any of the preceding arrangements; some of these will

be already apparent, and others are connected with effects to which we shall presently advert; to facilitate the experimental examination of such and other questions, Professor Daniell constructed what he termed a *dissected battery*; it is a circular arrangement of ten cells, each provided with a platinum and zinc plate (the latter being *amalgamated**) and which admit of being combined together in different ways. Over each platinum plate is an inverted and graduated glass tube, filled with the same dilute acid as the cell, in which the hydrogen gas disengaged may be collected and measured.

The following description and figures of this battery are from DANIELL'S *Introduction to the Study of Chemical Philosophy*, § 726, &c., and although the details involve a number of points of electro-chemical action which can only be adequately explained in the sequel, they have such important bearings, practical and theoretical, upon the whole subject, that I have thought it best to introduce them here.

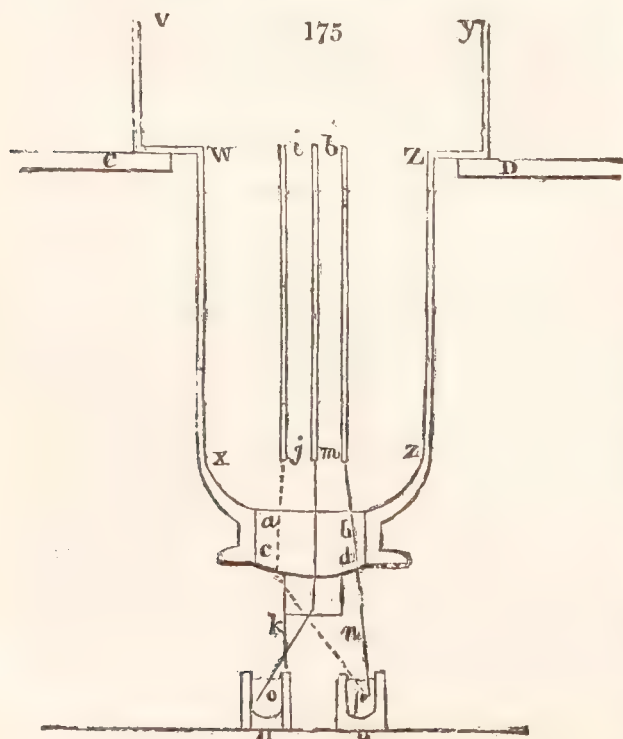


Fig. 175 represents a section of a single cell of this dissected battery. v w x z z y, is a glass cell resting by its wide rim in a circular hole in the stand c d. i j is a central zinc plate, connected by a wire passing through the stopper a b c d, with the mercury cup o, on either side of which is a platinum plate, both of which terminate by wires in the mercury cup, p. Either of these platinum

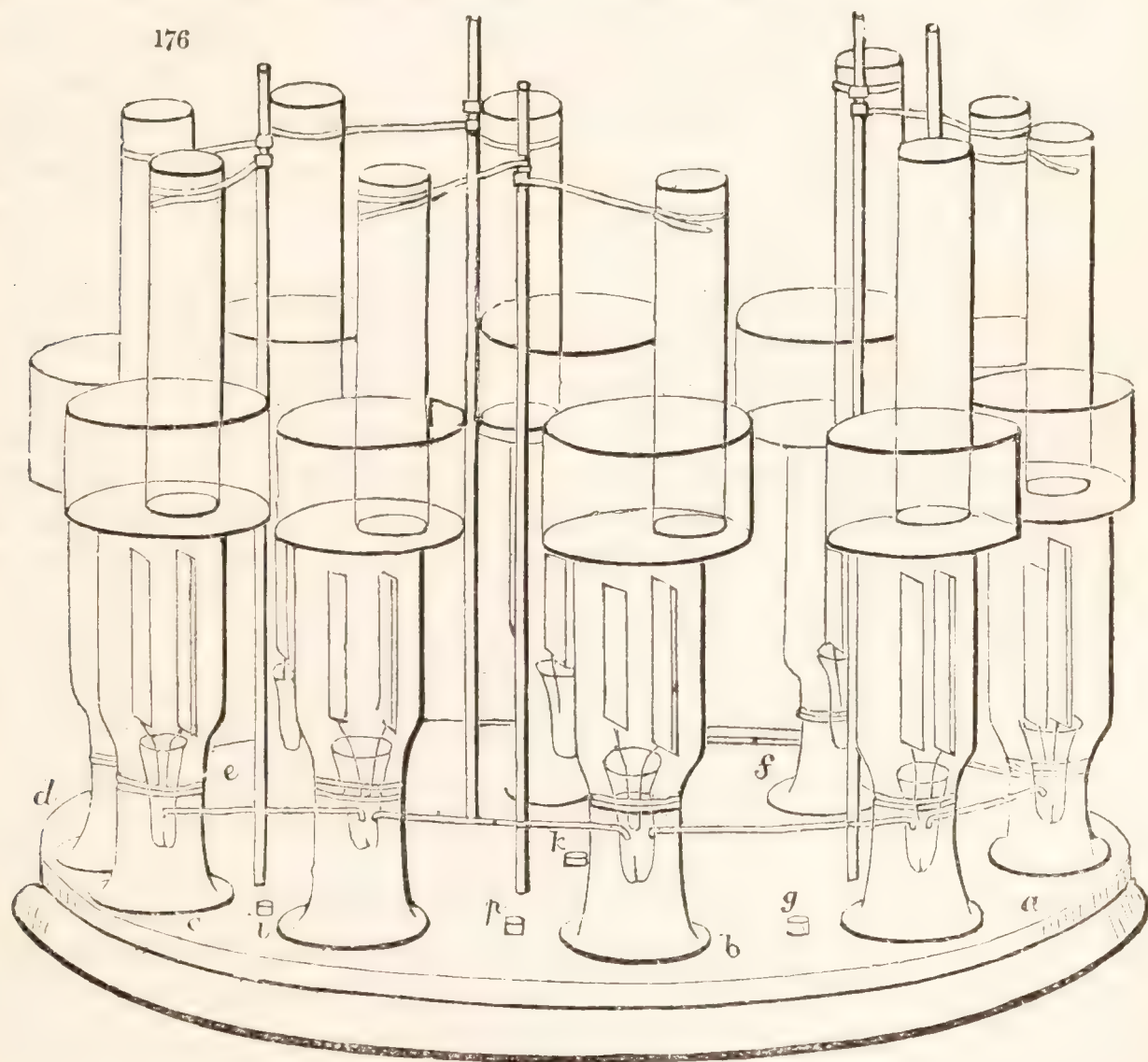
* The zinc plates are most conveniently *amalgamated* (that is, superficially combined with mercury) by putting some sulphuric acid diluted with 8 or 10 parts of water into a basin, and pouring into it a

little mercury: the zinc plates are then rubbed over with the acid and mercury by a piece of tow, till the surface becomes adequately amalgamated.

plates may be used singly by removing the other. The different connexions of the plates with the associated cells may easily be made by wires passing between the mercury cups.

The whole arrangement of the ten cells with the graduated glass jars is exhibited in the figure 176. They are placed upon a stand, *a b c d e f*, and the connexions between them are easily made and varied by the mercury cups, *i p k g*, &c.

Daniell observes, that however accurately it may be endeavoured to assimilate the cells to each other, it will be found that when connected as single circuits, either singly or together, the action of each will differ; but upon connecting them so as to form a single circular series, these inequalities will disappear, and the amount of gas from each in equal times will be equal. When the cells are combined together in pairs, two adjoining platinum plates being connected, and two corresponding zinc plates, and the five pairs are afterwards arranged in series by wires leading from each pair of zinc to the next pair of platinum, the irregularity of the action will again disappear. The arrangement is equivalent to a series of five plates of double the standard size, and the amount of force which circulates is determined by the least efficient pair.



“Leaving one pair of cells thus connected, if the others be disunited and recombined with it in single series, the effect will be that of a plate of double size, interposed in a compound circuit with eight single. The gas collected in each of the jars of the double cell will be exactly half of that in the several jars of the single cells; proving that the double plate

is reduced in efficiency to the exact standard of the single plates by its combination with them.

“In these arrangements every cell is a generating cell, and adds something to the quantity or intensity of the circulating force; and we see that unequal quantities cannot be generated and circulate in different parts of the same circuit. The effects of various retarding or opposing cells may be strikingly exemplified by the same apparatus. For this purpose the cells may be connected together in single series, substituting in one a platinum plate for the zinc; and the obstacle will then react upon the whole series; the action will be found to be reduced by more than one-third, and the quantities of gas collected from each generating cell will be exactly equal to that collected from the retarding cell. Upon repeating the experiment with a similar change in the next cell, the quantity of hydrogen in all the jars will be equal, but reduced to little more than one-tenth, and the current will be apparently stopped by three retarding cells to seven generating cells.”

Daniell also observes, that “when one of the zinc plates is removed from the regular series, and replaced by a platinum plate which has been previously coated with copper by the influence of hydrogen evolved in a circuit, the phenomena are striking and instructive. No gas will at first be evolved from the coppered plate, but it will oxidate, and the progress of the oxidation may be traced by the gradual blackening of its surface. The oxide, again, will be gradually dissolved, and the bright white surface of the platinum will make its appearance, and oxygen gas will begin to rise from it. At that moment the current will receive a check, which will be appreciable in all the air-jars.

“This mode of measuring the amount of current affinity by its chemical effects, has been applied in the construction of instruments, to which the name of Volta-meter has been given. They consist, in fact, of an independent closed cell, with two platinum plates, from which the gas may be conveniently collected and measured with great accuracy. They may be readily included in any circuit, and, although they check the current in all its parts, they accurately measure the amount which passes through them.

“When a Volta-meter is substituted for one of the ten cells, and the nine have a portion of nitric acid added to their charge, the quantity of hydrogen evolved from their conducting plates is greatly diminished, and becomes irregular; but the quantity of hydrogen indicated by the instrument is nearly treble that of the cells with their original charge.

“By observations made in this manner, it will be soon found that the action of such a compound circuit is not constant; and that it will gradually decline by a quantity which will be quite appreciable at intervals of five minutes. By breaking the connexion for a short period, its energy will be partially recovered, but will again decline as the action is renewed. Upon allowing the charge nearly to exhaust itself, it will be seen that the platinum plates have become incrustated with metallic zinc, originating, doubtless, from the oxide of zinc formed at the generating plates, and reduced by adhering hydrogen at the conducting plates. Its varying quantity and accumulation are amply sufficient to account for the

variation and ultimate annihilation of the circulating force; for zinc thus becomes opposed to zinc, and the circuit is destroyed. The momentary breaking of the connexion allows the acid to dissolve off the zinc, which being in contact with the platinum is most favorably disposed for this local action, and upon restoring it, the circulation returns to its first amount, but again speedily declines from the same cause*.”

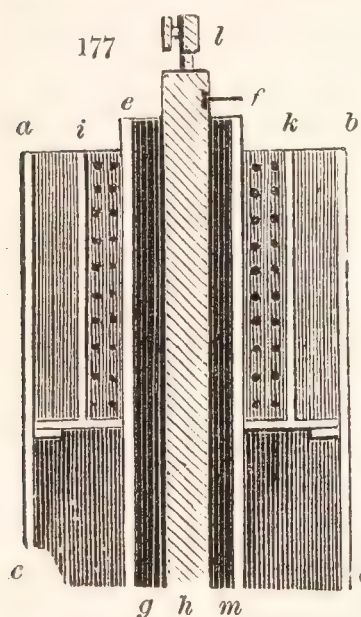
All the forms of voltaic apparatus above described, as well as others which have been devised, are open to the serious objection of inconstancy of action; many causes, some of which are obvious from the description just given of the “*dissected battery*,” co-operate to render their power uncertain, and in all it decreases in consequence of the decreasing chemical energy of the interposed liquid upon the generating plate; so that many researches, in which not only the continuous but the equal action of an electrical current during several hours was required, could not be undertaken. This obstacle to the progress of electro-chemical science has been obviated by the invention of the “*constant battery*,” contrived also by Professor Daniell. (*Phil. Trans.*, 1836, p. 117.) He describes it as follows. (*Introd.*, § 737.) “A cell of this battery consists of a cylinder of copper $3\frac{1}{2}$ inches in diameter, which experience has proved to afford the most advantageous distance between the generating and conducting surfaces, but which may vary in height according to the power which it is wished to obtain. A membranous tube, formed of the gullet of an ox, is hung in the centre by a collar and circular copper plate resting upon a rim placed near the top of the cylinder; and in this is suspended, by a wooden cross bar, a cylindrical rod of amalgamated zinc half an inch in diameter†. The cell is charged with a mixture of 8 parts of water and 1 of oil of vitriol which has been saturated with sulphate of copper; and portions of the solid salt are placed upon the upper copper plate, which is perforated like a colander for the purpose of keeping the solution always in a state of saturation. The internal tube is filled with the same acid mixture without the copper. A tube of porous earthenware may be substituted for the membrane with great convenience, but probably with some little loss of power. A number of such cells admit of being connected together very readily into a compound circuit, and

* There are many important points relating to the construction of the voltaic apparatus and to the theory of its action, which are necessarily omitted in this outline of the subject; such, for instance, as the relative dimensions of the generating as compared with the conducting plates of the series, and the various resistances to the circulation of the electricity. Upon these points I must refer the reader to the papers of Professors Faraday and Daniell, printed in the *Philosophical Transactions*; and to DANIELL'S *Introduction to the Study of Chemical Philosophy*, second edition. For the application of Ohm's mathematical formulæ to these inquiries, I may also refer to DANIELL'S *Introduction*, p. 487.

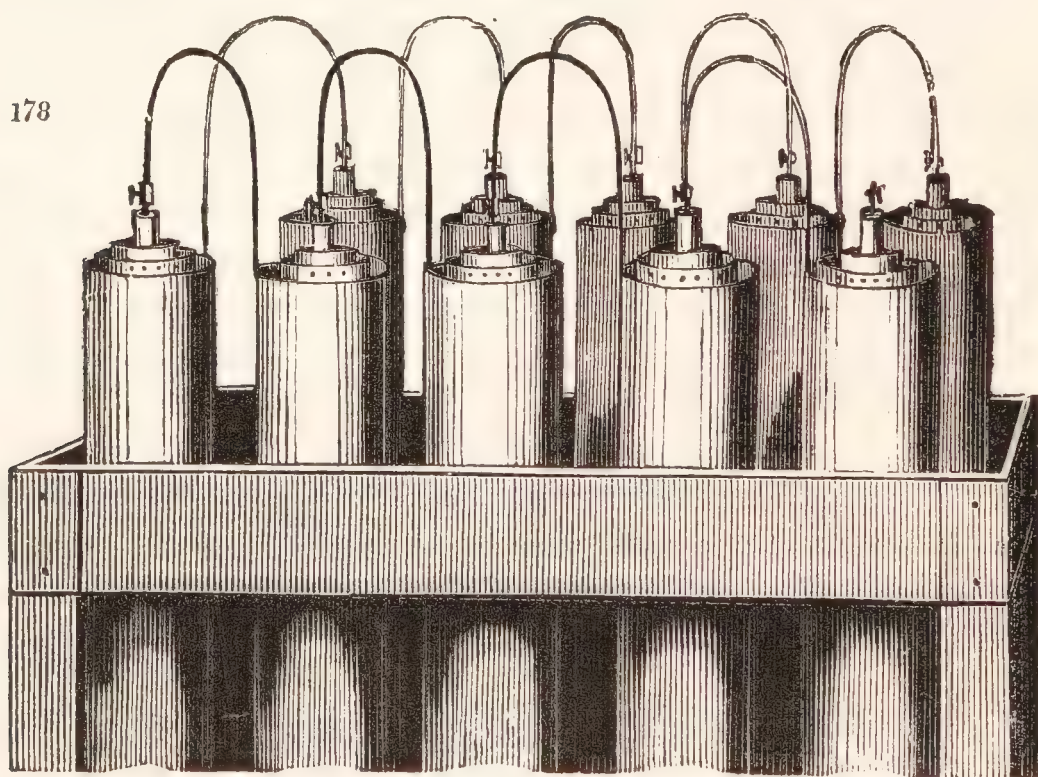
† In this battery the local action of the sulphuric acid on the zinc is prevented by its amalgamation, which causes a film of hydrogen to adhere to it so long as the circuit is incomplete. When complete, this hydrogen goes over to the copper, and by adhering to it interferes with the passage of the electricity; but the presence of the oxide of copper of the sulphate tends by secondary action to get rid of this hydrogen, which is employed in reducing the oxide; and successive films of metallic copper are thus thrown down upon the copper, and a clean metallic surface always preserved; while the deposition of copper upon the zinc plate (which would cause numerous small secondary circles) is prevented by the diaphragms.

will maintain a perfectly equal and steady current for many hours together, with a power far beyond that which can be produced by any other arrangement of a similar quantity of the metals."

A section of one of the cells of this constant battery is represented in the annexed cut (fig. 177); *a b c d* is a copper cylinder, in which is placed a smaller cylinder of porous earthenware. Upon the upper part of the copper cylinder rests a perforated colander, *i k*, through which the earthenware cylinder passes. *l m* is a cast rod of amalgamated zinc, resting upon the top of the interior cylinder by a cross piece of wood, and forming the axis of the arrangement. The cell is charged by pouring into the earthenware cylinder water acidulated with one-eighth part of its bulk of oil of vitriol, the space between the earthenware tube and the copper being filled with the same acidulated water saturated with sulphate of copper; and solid sulphate of copper being placed in the colander.



A number of such cells may be connected into a compound circuit, by wires attached to the copper cylinders, and fastened to the zinc rods by clamps and screws, as shown in fig. 178.

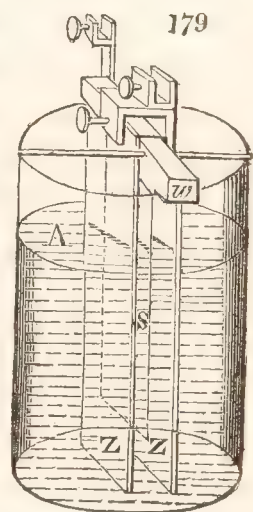


In the common battery, charged as it usually is with a mixture of sulphuric and nitric acid diluted with water, much local action takes place upon the zinc plates without contributing to the circulating forces, and whilst it is in action the oxide of zinc is reduced by the copper plate. In Daniell's battery these effects are avoided; the local action is prevented by the amalgamation of the zinc rod, and, upon the copper, nothing but copper can be precipitated.

Among the other modifications of the voltaic battery, which have been suggested, there are several which deserve the attention of the practical chemist, especially those called after their inventors, SMEE'S Battery and GROVE'S Battery.

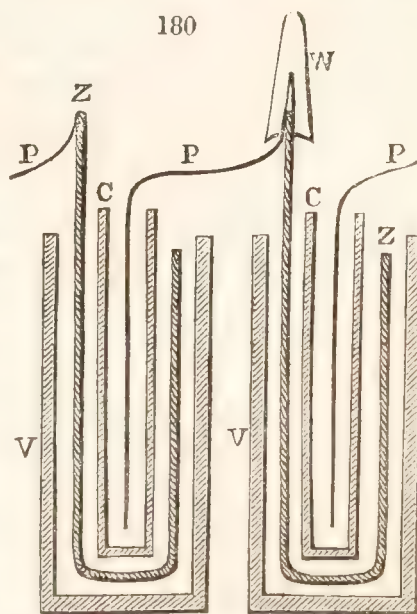
In Smee's battery (*Phil. Mag.*, 1840), a detailed description of which is given in his *Elements of Electro-metallurgy* (2d Ed. p. 23), the plates consist of amalgamated zinc, and either silver or platinum covered with a deposit of pulverulent platinum, by which a permanent rough surface is obtained, favoring the escape of the bubbles of hydrogen gas evolved upon it, the adhesion of which to the platinum or silver in their ordinary state, is an impediment to the action of the battery.

Platinized silver is generally employed, the platinum being thrown down by electro-chemical action upon the surface of the silver plate. A single cell of this battery is represented in fig. 179. A is an earthenware or glass vessel, containing the dilute acid (1 of sulphuric acid to 7 of water); *w* is a bar of wood to which the platinum plate *s* is attached: *z z* are two plates of amalgamated zinc, secured to the bar by the binding-screw *b*, and another binding-screw is soldered to the platinized plate for the convenience of making connexions by wires. When a series of these batteries are employed, they are generally adapted to a porcelain trough similar to that already described. (fig. 173.) For many purposes of experiment, and especially in electro-metallurgy, these batteries are extremely convenient.



The *Nitric acid Battery* of Professor Grove (*Phil. Mag.*, 1839 and 1841, vol. xviii. 234) is an extremely valuable instrument, both to the lecturer and the experimentalist: it combines great power both of quantity and intensity: it occupies little space; it is free from the inconveniences of local action, and therefore so far a *constant battery*; and is upon the whole more economical than any other form of the apparatus combining the same attributes. The sections of two cells of this battery are represented in the annexed cut (fig. 180).

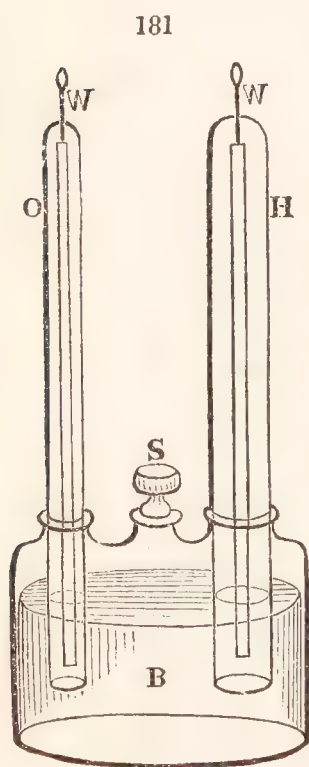
The outer vessel *v* is a flat cell of glazed porcelain, containing within it another similarly shaped, but smaller and thinner cell *c* of porous earthenware. A flat plate of amalgamated zinc, *z*, is bent so as to receive the porous cell; a plate of thick platinum foil, *p*, being contained within the latter, and long enough to extend to the projecting end of the zinc plate of the next cell, perfect contact being there preserved by the cleft piece of wood *w*. The inner porous cell is charged with strong nitric acid: the outer porcelain cell with a mixture of 1 part of oil of vitriol and 6 of water. The zinc being amalgamated, there is, in this apparatus, as in Daniell's, no chemical action till the current passes; and then the evolved hydrogen is suppressed by the nitric acid, which it deoxidizes, and converts into nitrous acid, gradually changing its color to yellow, green, and blue, and nitrous vapors are after a time evolved, which may be easily carried off. By occasionally stopping the current, any violent action of this kind may be prevented, and this it is necessary to attend to, lest the effervescence should



occasion the throwing over of part of the nitric acid into the outer cell. From four to twenty of these cells are sufficient for all the purposes of research and illustration, such as the ignition of wires and of charcoal, chemical decompositions, &c., and are by far the most convenient form of battery for the lecture-table.

It has been proposed to substitute various forms of indurated carbon, and plumbago, for the platinum in the construction of these batteries (COOPER, *Phil. Mag.*, Jan. 1840; BUNSEN, *Electr. Mag.*, I. 16); but hitherto so much inconvenience has attended the use of such materials, that they have not been generally adopted.

Professor Grove has invented another voltaic arrangement, termed a *gas battery* (*Phil. Trans.*, 1843), which, theoretically considered, is of much interest. The action of preceding arrangements may generally be referred to the *decomposition* of water, the oxygen of which combines with the zinc, and the hydrogen is either evolved or otherwise disposed of. In the gas battery the converse action takes place, and the electricity is apparently produced by the *combination* of oxygen with hydrogen, or by the formation of water. One of the forms of a cell of this battery is shown in fig. 181. B is a bottle with three necks; the central opening may be occasionally closed by a stopper s, and into each of the others the tubes o and h are fitted by grinding;



each tube includes a strip of platinized platinum, connected with the wires w, and the tube h is double the capacity of o. The apparatus is charged by filling the vessel and tubes with dilute sulphuric acid, and then by a bladder and bent tube throwing up hydrogen into h, and oxygen into o. If the wires w be now connected with a galvanoscope, an electrical current is indicated; and when several series are combined, by connecting the oxygen tube of one cell with the hydrogen tube of the next, and so on, while the terminal wires are connected with a voltameter, it is found that the oxygen and hydrogen evolved is exactly equal to the respective quantities of those gases absorbed by the act of combination in each tube. It would appear, therefore, that when this circuit is closed, an atom of oxygen combines with one of hydrogen in the atom of water in contact with it; that the oxygen of this atom of water combines with the hydrogen of

the next, and so on, till the last atom of oxygen coming into contact with the hydrogen in the tube h there combines with it, so that ultimately an atom of water is formed by the union of an atom of hydrogen from one tube with an atom of oxygen from the other, and *vice versâ*. This operation continues till the gases are consumed; and the water *decomposed* in the voltameter, is, as we have said, equal to that *composed* in each cell. Some other gases may be occasionally substituted for the hydrogen and oxygen.

The *electro-polar* state of the voltaic battery, that is, the state of its extremities when unconnected, resembles that of De Luc's column, and although the intensity of its electricity is in general feeble, it may be rendered evident by a gold-leaf electrometer, or by the condenser, or by the form of electrometer represented in fig. 165, in which one of the

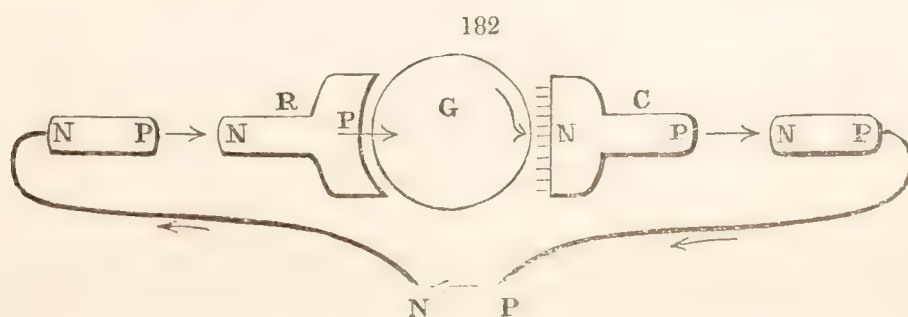
leaves being connected with one extremity, and the other with the opposite extremity of the battery, will become mutually attractive. These effects of *tension*, as belonging to the voltaic pile, are best observed when the alternations are very numerous, the troughs well insulated, the plates perfectly clean, and charged, not with acid, but with water. This I had a good opportunity of witnessing in a large battery of 2000 double plates, constructed, under the direction of Mr. Pepys, for the London Institution. When quite new and clean, it was insulated upon wine-bottles, and charged with river-water; it gave a shock resembling that of a Leyden phial, and required some time to recharge itself; the sparks were feeble, but it was permanently active upon the electrometer, and a pith-ball attached by a thread to its positive pole was attracted by another attached to its negative pole; it also communicated a charge to a Leyden battery, when the wires from its extremities were respectively connected with the inner and outer surfaces of the jars. But with all this manifestation of intensity, the energies depending upon *quantity* were very feeble so long as it was only charged with water.

Mr. Crosse and Mr. Gassiot have constructed extensive water batteries, that of Mr. Gassiot consisting of 3520 pairs; the cells are glass varnished with shell-lac and well insulated; the metals are cylinders of zinc and copper, kept apart by string; the exciting liquid, distilled water. With this arrangement, sparks pass *before* the contact of the poles, and the phenomena of tension are all very evident. (*Phil. Trans.*, 1840.)

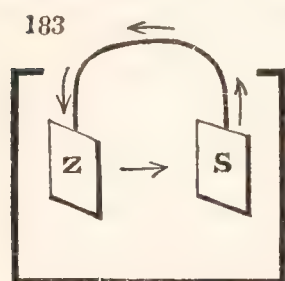
Much ambiguity occasionally arises out of the indefinite meaning attached to the terms *positive* and *negative*, in speaking of the direction of the electric current, and in reference to the elements of the voltaic battery: I shall, therefore, endeavour here to define those terms in the sense in which I always employ them.

Whenever a body is in the electric state it is either POSITIVE (*as glass rubbed by silk*), or NEGATIVE (*as resin rubbed by flannel*), to every other body. If in the *positive* state in respect to these other bodies, electricity tends to pass from it to them; (that is, according to the conventional phrases now in use, and about which there can be no mistake if we turn from them to the facts which they are intended to represent;) and if in the *negative* state with respect to them, electricity tends to pass from them to it. So also the passage or *current* of electricity (the direction of which may be determined by the effects which it produces) is always *from* the positive *to* the negative, whether we speak of masses of matter, or of particles, or of the parts of wires, liquids, or other media, through which the electricity is moving.

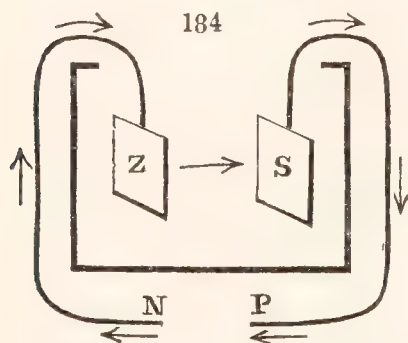
In the common or frictional electrical machine, the rubber R (fig. 182) imparts electricity to the glass G, so that the surface of the rubber at P is



positive to the rubbing glass, but *negative* elsewhere to bodies brought towards it through the atmosphere. The conductor *c* is *negative* at *N* in relation to the excited glass, or in a condition to receive electricity; and having received electricity, it becomes *positive* at *P* and elsewhere, in relation to bodies to which it can give electricity. Speaking, therefore, of the electrical *current*, it may be said to pass from the surface *P* of *R* over to *N* of *c*, and from *P* of *c* forward in the direction of the darts, so that *P* would be the *positive pole* (anode or anelectrode) and *N* the *negative pole* (cathode or cathelectrode) of the conductors *R* and *c*, and so on in regard to the other conductors *N P*, &c.

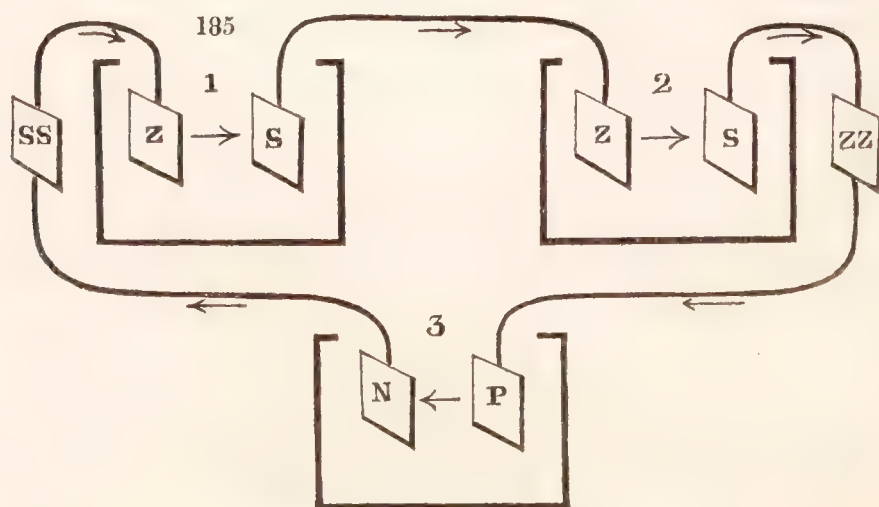


and *s* the *negative* surface in relation to *z* through the acid.



In the arrangement (fig. 184) the current would pass from *z*, or the *positive* surface, to *s*, or the *negative* surface, and from *s* would traverse in the direction of the darts; so that *P* would represent the *positive pole*, or the *anode*; and *N* the *negative pole*, or the *cathode*. The *active* metal is always the *positive*, or generating metal, upon which oxygen, chlorine, and other *anions* (electro-negative bodies) are evolved. The *inactive* or *passive*, or as it is sometimes called, *conducting* metal, is *negative*, and upon it hydrogen and the metals and other *cations* (electro-positive bodies) are evolved, in all cases of electrolytic action. If, in these arrangements, a liquid were substituted for the dilute sulphuric acid, which would act upon the silver and not upon the zinc, the current would then be inverted, and the *silver* become the generating or *positive* metal, and the *zinc* the receiving or *negative* metal.

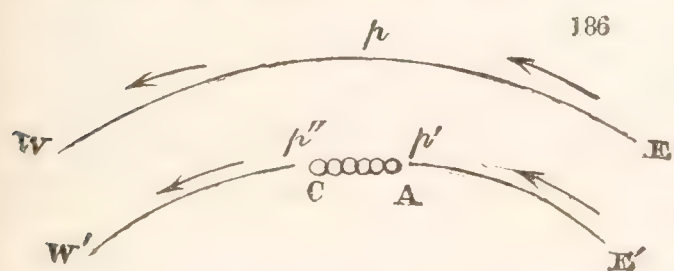
In fig. 185, which represents a compound circle, the direction of the current is from *z* to *s* in vessel 1 across the dilute acid, and from this *s* to



z in vessel 2, through the connecting wire; again from *z* to *s* through the liquid in vessel 2, and from *P* to *N* in vessel 3, and onwards from *N*

through the connecting wire to *z* in vessel 1. It is here assumed that the metallic plates in vessels 1 and 2 are respectively zinc and silver immersed in the dilute acid, and that in vessel 3 they are of platinum immersed in the same acid. In the vessels 1 and 2, the oxygen of the electrolyte combines with, and tends to the solution of the zinc, which has therefore been called the *active*, and is the *positive* metal; the hydrogen escapes from the surface of the silver, which is not acted upon, and which is therefore the *passive* or *negative* metal. In vessel 3, where the plates are of platinum, neither is acted on, but oxygen is given off upon *p* (which corresponds to *z* in vessels 1 and 2), because it is the *positive* pole; and hydrogen is given off upon *n* (corresponding to *s* in vessels 1 and 2), it being the *negative* pole. The extra plates *ss* and *zz* in the ordinary construction of the apparatus show why such zinc end of the arrangement has often been designated as the *positive* end, and the corresponding silver end as the negative. These extra plates are merely attached for the convenience of carrying on the series, and as far as the present diagram is concerned, might obviously be dispensed with.

The termination of the conductors or wires connected with the opposite ends of the voltaic battery, are commonly termed its positive and negative *poles*, a term which becomes objectionable when we ascribe to them certain attractive and repulsive powers, and other effects which are the result, not of forces residing in the *poles*, but of the passage or current of electricity; the *poles*, as they are usually termed, are merely the surfaces by which the electricity comes in and goes out; they act simply as a *path* or door to the electric current: in place of the term *pole*, therefore, Faraday uses *electrode* (from *ηλεκτρον* and *οδος* a way) meaning thereby that substance or surface, whether of air, water, or metal, which bounds the extent of the decomposing matter, or electrolyte, in the direction of the electric current. The place at which the electricity enters the electrolyte, he terms the *anode*, that at which it leaves it, *cathode*, in reference, if we



suppose the current of electricity to follow the passage of the sun, (that is, to pass from east to west,) in its rising and setting. If, for instance, we suppose a current of electricity traversing a wire in the direction of the darts in the annexed diagram, and entering at *E*, then, on separating the wire at *p*, *p'* *p''* would become its *poles* or *electrodes*; and *p'* would be the positive, or emitting electrode, or the *anelectrode*; and *p''* the negative or receiving electrode, or the *cathodelectrode*. *E* being the wire which (in common language) is connected with the zinc end, and *w'* that connected with the copper end of the battery. Such, therefore, is the meaning which must be attached to the term *poles*. And, supposing the chain of circles *c* *A* to represent the *electrolyte*, *A* would be its *anode*, and *c* its *cathode*. By some, the plate which occupies the place of the generating plate in the battery, has been called the *zincode*, and the conducting plate has been distinguished as the *platinode*.

When a powerful voltaic battery is in good action, the following effects are perceived. On making the communication between its extremities

by charcoal points, a vivid light and intense heat are produced; and, on



slowly withdrawing the points from each other, a constant current of electricity passes between them; producing an arc of light of such intensity as scarcely to

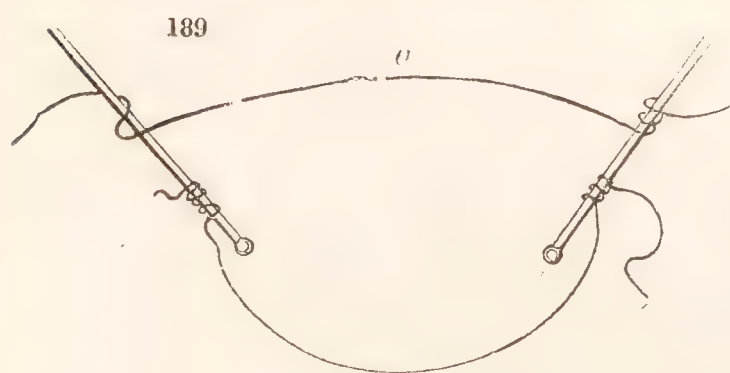
be borne by the unprotected eye, and of the form represented by figure 187. When the charcoal points are gradually withdrawn from each other in a vessel exhausted of the greater portion of its air, as in the apparatus represented by figure 188, the effect is even more brilliant. (On the *intensity* of this light, see MM. FIZEAU and FOUCAULT, *Ann. Ch. et Ph.*, July, 1844.)



The extreme intensity of the *heat*, in this arc of flame, is rendered evident by exposing in it very difficultly fusible substances, which readily melt: even substances infusible by almost all ordinary methods are thus liquified.

When gold, silver, zinc, or copper leaf are interposed between the poles, they are ignited and burned; and fine wires are heated red or white-hot, according to their lengths and diameters: with an iron wire the combustion is extremely brilliant. All these effects upon good conductors, depending chiefly upon *quantity* of electricity, are most effectively produced by *large plates*. A formidable battery of this kind was constructed by Mr. Children. (*Phil. Trans.*, 1815.) The plates were two feet eight inches wide, and six feet high, the copper being opposed to both surfaces of the zinc: they were properly fastened to a beam of wood, suspended by counterpoises from the ceiling of the laboratory, so as to be readily and safely immersed into, or removed from, the cells of acid, which were twenty-one in number, and their united capacities amounted to 945 gallons. A leaden pipe, three-fourths of an inch diameter, was attached to the extreme plate at either end, and immersed into separate basins of mercury, by means of which perfect metallic contact was ensured. The charge consisted of a mixture of nitric and sulphuric acids, with thirty, or occasionally only twenty, parts of water.

When the poles of this arrangement were united, as shown in figure



189, by a platinum wire eleven-hundredths of an inch diameter, it became red-hot for a length of five feet six inches. In the same way, it ignited eight feet six inches of the same wire of forty-four hundredths of an inch; and a bar of platinum, one-sixth of an inch square, and two and a quarter long,

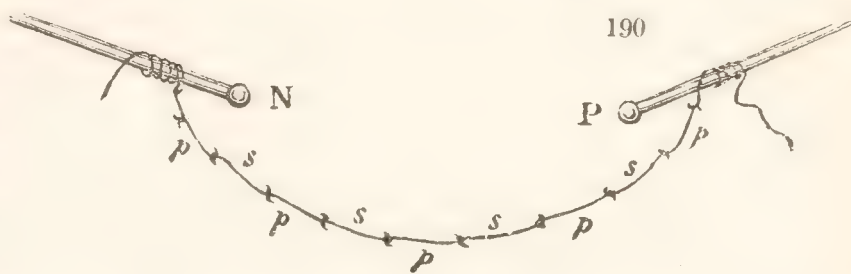
was not only heated to bright redness, but fused at the end. A number of intractable and very difficultly fusible substances, submitted to the high temperature occasioned by the discharge of this battery through

charcoal points, exhibited indications of the most intense heat; but perhaps the most interesting results were obtained by transmitting the electricity through *different* metallic wires. For this purpose either single wires, or wires of dissimilar metals, were used, of equal diameter and length: one end of each was in contact with one of the basins of mercury communicating with the poles of the battery, and the other end bent to an angle, and the wires connected continuously by hooking them together. The length of each wire was eight inches, and the diameter one-thirtieth of an inch.

Platinum and gold being thus connected, the platinum was made red-hot, whilst the gold remained unaffected. With a similar arrangement of gold and silver wires, the gold was ignited, the silver not. With gold and copper, both metals were equally heated to redness. With gold and iron, the iron was ignited, the gold not affected. With alternations of platinum and silver three times repeated, all the platinum wires were ignited but none of the silver.

These experiments, which may be made with a less powerful battery, are extremely beautiful and instructive, especially the last: for this purpose select some fine silver and platinum wire, and cut it into lengths of about two inches; then form a continuous wire by joining these lengths

endways, in alternate order, and suspend it in a festoon between two thick copper wires, forming the poles of the battery, as in fig. 190, having previously tem-



porarily united these poles by a thick copper wire, as is shown at *a* in fig. 189; on removing the latter, the electricity traverses the compound wire, and occasions the ignition of the platinum portions of it only, the silver being merely heated. The object of uniting the poles by a thick copper wire, whilst the compound wire is being attached, is to prevent the sudden fusion of the latter at the point of contact, which often happens when this precaution is not taken.

The cause of these appearances was referred by Mr. Children to the different *conducting powers* of the metals; that platinum conducts electricity less perfectly than silver, and that, consequently, the electricity, meeting with greater resistance in its passage through that metal, makes it red or even white hot; while, on the other hand, passing with comparative facility through the silver, it is much less heated. It is obvious that this explanation rests upon the supposition, that resistance to the passage of electricity occasions the development of heat; and as this must be inversely as the conducting power, when any two of the wires, connected continuously, are placed in the circuit, that which is the worst conductor must be most heated; and silver, therefore, which is the best conductor, is not heated red when connected with any other metal.

Mr. Daniell has described (*Phil. Trans.*, 1839, p. 92) the powerful effects of a constant battery of 70 cells. The flame formed a continuous arch of three-fourths of an inch, which striking distance was not increased in vacuo: it was dangerous to the eye, even when protected by colored glasses, producing, when reflected from an imperfect parabolic

mirror in a lantern, inflammation and a scorching like that of the sun: the rays were collected into a focus by a glass lens, and readily burned paper at many feet from their source. The heat was intolerable to the hand when held near the lantern. Paper, steeped in nitrate of silver, was quickly discolored in the light. The transfer of charcoal from the positive to the negative electrode, produced a cavity in the former and a protuberance upon the latter; and when a platinum rod was substituted for the charcoal forming the negative pole, the transfer from the charcoal at the positive pole still took place, and the metal was coated with carbon, beautifully moulded to its extremity. When this arrangement was reversed, particles of platinum were transferred, and the charcoal on the negative pole became covered with globules of the fused metal. No spark could be made to pass from one electrode to the other, (even when separated by the smallest stratum of air,) previously to the electrodes having been brought into contact; but when two brass balls formed the poles within a very minute distance of each other, and the spark of a small Leyden jar was passed between them, then the battery current was immediately established, and the balls burned*. Mr. Daniell supposes that the Leyden discharge transferred the conducting matter (particles of brass in this case), which was essential to the existence of the voltaic flame, and which was afterwards supplied by its own energy. The arch of flame was attracted and repelled by the poles of a magnet, and it rotated when the flame was drawn from the pole of the magnet itself included in the circuit. The intensity of heat on the side of the positive electrode was much greater than that of the negative. When two stout copper wires of one-fifth of an inch diameter were connected with the extremities of the battery, and held across each other, so that the flame passed between them, the wire at the positive end became red-hot, while the other remained comparatively cool. A bar of platinum, one-eighth of an inch square, melted into globules in the former situation, but showed no signs of fusion in the negative electrode. When the positive electrode was formed of the hard carbon taken from a gas-retort, and a cavity ground in it, the most infusible metals placed in it were melted in considerable quantities. Rhodium, the native alloy of iridium and osmium, the native ore of platinum, and titanium were thus fused.

The quantity and the intensity of the electricity in the voltaic pile are respectively modified, as has been stated, by the size and number of the plates, and by the action of the intervening liquid. When the zinc plates are perfectly clean, pure water produces certain electrical effects; these are considerably modified by dissolving common salt in it, or employing other saline liquids; but the dilute acids are best calculated to increase them. If, for instance, we charge three single troughs, each of ten pairs of plates, with water, brine, and very dilute nitric acid, the first will show scarcely any signs of electricity; the second will give a feeble spark and shock; the third will ignite the charcoal points, producing a continuous star of brilliant light. The first will not decompose

* In reference to the question whether a spark can be obtained before the circuit of the voltaic battery is complete, and also for a description of the brilliant effects of a

constant battery of 320 series, see two papers by Mr. Gassiot, *Phil. Trans.*, 1839, p. 183, and *Transactions of the Electrical Society*.

water; the second does it feebly; the third rapidly. It is obvious, therefore, that with a small number of plates *highly* charged (that is, with dilute acid), we obtain effects equivalent to those of a larger series *feebly* charged; the experimentalist must therefore regulate the strength of the charge according to the number of plates, and the effects which are required. (See FARADAY'S *Researches*, Series X.)

All the effects of *electrical intensity*, such as affecting electrometers, giving shocks, charging jars, decomposing water and saline solutions, and so forth, are, as above remarked, increased by increasing the *number* of the plates, but (*the charge being in both cases the same*) the production of *quantity* of electricity becomes dependent upon the extent of surface of the plates. Thus, if a battery composed of thirty pairs of plates, *two inches square*, be compared with another battery of thirty pairs of *twelve inches square*, scarcely any difference will be perceived in their effects upon *bad* and imperfect conductors; their powers of decomposing water and of giving shocks will be nearly similar; but upon *good* conductors, the effects of the large plates will be very distinct from those of the small ones; the spark, and arc of light between charcoal points, will be much more intense and extensive; and when the charge is transmitted through a fine platinum wire, much of it will be heated red-hot; an effect which the small plates are quite inadequate to produce.

The following experiments are adduced by Sir H. Davy, as illustrating these relative effects of *quantity* and *intensity* in the voltaic apparatus:—

Immerse the platinum wires, connected with the extremities of a charged battery composed of *twelve-inch* plates, into water, and it will be found that the evolution of gas is nearly the same as that occasioned by a similar number of *two-inch* plates. Apply the moistened fingers to the wires, and the shock will be the same as if there were no connexion by the water. While the circuit exists through the human body and through the water, let a wire, attached to a thin slip of charcoal, be made to connect the poles of the battery, and the charcoal will become vividly ignited. The water and the animal substance discharge the electricity of a surface probably not superior to their own surface of contact with the metals; the wires and charcoal discharge all the residuary electricity of the plates; and if a similar experiment be made upon plates of an inch square, there will scarcely be any sensation when the hands are made to connect the ends of the battery, a circuit being previously made through water; and no spark when charcoal is made the medium of connexion, imperfect conductors having been previously applied.

In all the preceding arrangements two metals and a fluid are concerned in the evolution of the electric current, and in the case of zinc, acid, and copper, the zinc is termed the generating plate, being that which is oxidized, and the copper the conveying or conducting plate; but, were we to use liquids acting chemically upon the copper and not upon the zinc, the direction of the current would be inverted, and the copper become the generator, and the zinc the conductor.

It is, however, by no means essential that two metals should be employed to obtain an electric current; for if only one metal be used, different parts of which are unequally acted on by an acid, or other fluid, electricity will be evolved according to the same law; the portion of the

metal most acted on becoming the generator or positive element : thus a current is established when a plate of new and clean zinc and one of oxidized or corroded zinc are used, or when one of the plates is of cast and the other of rolled zinc. Upon the same principle, when a strip of copper, clean at one end and corroded at the other, is immersed in dilute nitric acid, an electric current is produced; in all these cases the surface which is most open to chemical action, corresponds to the zinc, and that least so, to the silver or copper of the simple circle above described.

An electric current is also manifested when a single plate of metal of uniform surface is acted upon by two fluids exerting distinct chemical actions upon it. If, for instance, the vessel be half filled with a strong solution of sulphate of copper, and then carefully filled up with dilute sulphuric acid, so that the latter may lie upon but not mix with it, a plate of iron immersed will be so acted on as to produce an electric current, the upper part becoming the equivalent of the zinc, and the lower that of the copper in the simple circle. A plate of copper immersed in the same way will produce a similar effect, and metallic copper in a crystalline form will be deposited upon its lower end. These, and similar phenomena in reference to the source of power in the voltaic pile, have been investigated by Faraday, in the sixteenth and seventeenth Series of his "Experimental Researches in Electricity." (*Phil. Trans.*, 1840.)

§ 12. ELECTROLYSIS.

THE *chemical powers*, as they are usually termed, of the voltaic pile were first observed in regard to the decomposition of water and certain saline solutions, by Messrs. Nicholson and Carlisle, in the year 1800, (*Phil. Mag.*, vii., and *NICHOLSON'S Jour.*, 4to., iv. 183); they were then more accurately investigated in 1803, by Hisinger and Berzelius, (*GEHLEN'S Jour.*, i. 115,) and, in 1807, Sir H. Davy communicated his celebrated lecture "On some chemical agencies of Electricity" to the Royal Society, in which the electro-chemical powers of the pile were more minutely examined, and which formed the groundwork of the brilliant discoveries to which he was soon afterwards led. There were, however, many important phenomena, more especially those connected with the development of electricity by chemical action, and with the theory of electro-chemical decomposition, which Sir H. Davy, and others, whose researches have enlightened this difficult department of experimental science, either left unexplored, or insufficiently and unsatisfactorily explained : these have engaged the attention of many later and acute experimentalists, and more especially of Professor Faraday, whose "Experimental Researches in Electricity," published in a succession of papers, communicated to the Royal Society (*Phil. Trans.*, 1832 to 1846), contain the results of his labors in reference to this branch of knowledge. They have not only, as our preceding pages have shown, explained and enlightened much that was before unintelligible and obscure in regard to statical electricity, but have also stamped a new character upon electrical as connected with chemical science; in point of originality in devising experiments, skill in carrying them into effect, and perspicuity in tracing out and unravelling the complicated relations and bearings of the new truths which are elicited, Faraday stands, if not unrivalled, at least unsurpassed.

When the electrodes of the voltaic battery are brought near to each other in certain liquids, such, for instance, as *acidulated water* and *saline solutions*; or, in other words, when these liquids are made part of the electric circuit, so that the current of electricity passes through them, *decomposition* ensues; that is, certain elements are evolved in obedience to certain laws; the water, for instance, yields *oxygen* and *hydrogen*; and the neutral salts yield *acids* and *alkalis*. In these cases, the ultimate and proximate elements appear at the electrodes; not indiscriminately, or indifferently; but *oxygen* and acids are developed at the *anode*, or surface at which the electricity enters the electrolyte; and *hydrogen*, and alkaline bases, at the *cathode*, or surface at which the electric current leaves the body under decomposition.

As the elements of substances thus electrically decomposed are uniformly separated at one or other electrode, it has been assumed that the natural or inherent electricity of such elements is the antagonist of that supposed to belong to the surface at which they appear; in conformity to the law already laid down, "that bodies dissimilarly electrified attract each other;" it has further been assumed, that the elements of compounds are held together by certain electro-chemical forces, more feeble than those belonging to the pile, and that they are consequently overcome by such superior power; that when substances (or their atoms) are similarly electrical they will refuse to combine; and that substances which, in their ordinary states, exhibit no mutual affinities, may be made to enter into combination by communicating to them dissimilar electrical states.

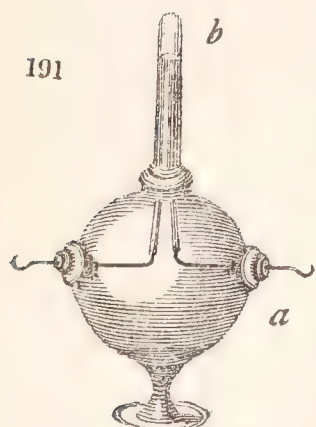
But in classing bodies according to their electrical relations, it is important to state those relations, without involving the expression of hypothetical views, and to this end, Mr. Faraday uses the following terms. All substances susceptible of *direct* decomposition by the electric current, he calls, as already stated, *electrolytes*; and for the term *electro-chemically decomposed*, he substitutes *electrolysed*. Those elements of the electrolyte which are evolved at the *anode*, he terms *anions*, and those which are evolved at the *cathode*, *cations*, (*ανιον*, that which goes *upwards*; *κατιον*, that which goes *downwards*, in reference to *anode* and *cathode* already defined,) and when these are spoken of together, they are called *ions*: thus, when acidulated water is *electrolysed*, two *ions* are evolved, oxygen and hydrogen, the former being an *anion*, the latter a *cation*.

I shall now proceed to a few experimental illustrations of *electrolysis*, or *electro-chemical decomposition*, and afterwards consider the general laws which have been deduced from them*.

* The terms positive and negative *pole* are used in speaking of electro-chemical action in two senses: they are frequently employed in reference to certain supposed attractive and repulsive powers belonging to them, and with the same meaning as in speaking of quiescent electricity; but, in reference to electricity in motion, they refer to the surface or passage by which the electricity passes into, and out of the body, under decomposition. In the case,

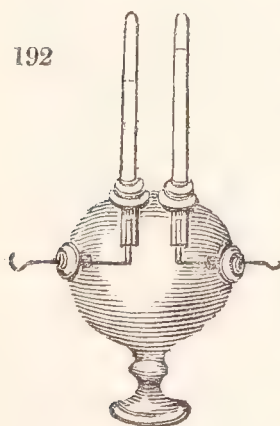
for instance, of a current of electricity traversing a wire or any other substance, and passing from east to west, if we may make a break in it, the eastern side of the divided part becomes the positive pole, and the western the negative pole, as may be learned from the diagram fig. 186. But this explanation only applies to the hypothesis of a single electric fluid, traversing the conductor in a given direction: if we assume *two* electric fluids, we must suppose that

If two platinum electrodes be brought near each other in water acidulated by sulphuric acid, a stream of gas will issue from each, which in an apparatus similar to fig. 191, may be collected, and examined. *a* is a glass globe with three apertures; two of these (on the



sides) are fitted with corks perforated by glass tubes of such length as to approach the centre of the globe, and traversed by platinum wires, which are flattened out into plates at the ends, and turned upwards, within a tenth of an inch of each other. The tube *b* is inverted into the neck of the globe, in which a notch is filed, so as to admit of the oozing of a portion of the liquid. This apparatus is then filled with the acidulated water, and the hooked ends of the platinum

wires made to communicate with the conducting wires of the voltaic apparatus; gas immediately bubbles up into the tube, and the displaced liquid trickles out at the neck of the globe. It will be observed, that twice the quantity of gas escapes at the negative pole, or the *cathode*, as compared with that at the positive pole, or at the *anode*: and the tube will be found to contain a mixture of *hydrogen* and *oxygen* gases, in the proportion of *two* volumes of the *former* liberated at the *cathode*, or *negative pole*, and *one* of the *latter* at the *anode* or *positive pole*. If a lighted candle be brought to the mouth of the tube, the mixed gases explode and again produce water.



By a modification of this arrangement, the evolved gases may be collected in separate tubes; as, for instance, if we employ a globe with two orifices (fig. 192), each having a tube so adapted as separately to receive the gas from each pole. It will then be seen that *two* volumes of *hydrogen* gas, and *one* volume of *oxygen* gas, are respectively collected in the tubes inverted over the *negative* and the *positive* poles. Upon the approach of a taper, the hydrogen gas will burn quietly with a blue lambent flame; and the oxygen may be recognised by immersing into it the glowing wick of a small piece of green taper, which will instantly kindle

into flame*.

These experiments are here merely adduced in illustration of the decomposing or electrolytic powers of the current; they show that, under

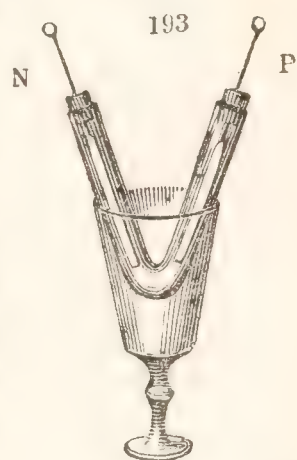
they traverse the wire connecting the extremities of the battery in *opposite* directions, in which case, the positive electric fluid must be assumed to issue from the positive pole, and re-enter by the negative; and the negative fluid to issue from the negative pole, and re-enter by the positive. Professor Daniell calls the positive pole, or the *anode*, the *zincode*; and the negative pole or *cathode*, the *platinode*; the former being the electrode, which in the regular battery would be constructed of zinc, and the latter of platinum. Professor Graham uses the terms *zincous* and *chlo-*

rous poles, the former having the characteristic affinities of zinc, for oxygen, chlorine, &c., the latter those of chlorine, for hydrogen and the metals.

* In these experiments we employ water, to which a small portion of sulphuric acid has been added, for if *perfectly pure water* be used, it resists the passage of the electric current to such an extent as to render it doubtful whether in that state it be or be not an electrolyte; the electrolysis of common water probably depends upon the saline matter which it holds in solution. (See the sections on *Water* and *Sulphuric Acid*.)

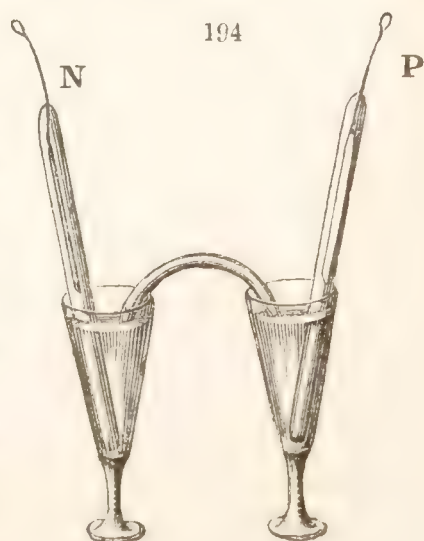
whatever circumstances water is decomposed, the hydrogen is evolved at the cathode, (or at the negative pole,) and the oxygen at the anode, (or positive pole). They are, however, further important, as establishing the composition of water; for, if we reduce the volumes of the gases to their respective *weights*, we shall find that, the volume of hydrogen being = 1, the half volume of oxygen will be = 8, and, consequently, nine parts of water will consist of one part *by weight* of hydrogen, and eight parts *by weight* of oxygen, for the specific gravity of oxygen to hydrogen is as 16 to 1.

If, in these experiments, we employ water containing neutral salts, we find that they are also decomposed, and that their elements are also separated according to certain laws. This may be strikingly illustrated by dissolving some such salt in water, and electrifying the solution, as in the following experiment. Provide a piece of glass tube, bent at an angle, and placed in a wine-glass, to serve for its foot or support. Fill this syphon with the blue infusion obtained by macerating the leaves of the red cabbage in boiling water, and put into it a few crystals of *sulphate of soda*; then place a strip of platinum foil in each leg of the syphon, taking care that they do not come into contact at the elbow of the tube, and connect one of these with the negative, and the other with the positive, pole of the pile: in a few minutes the blue color will be changed to *green* in the negative side, and to *red* in the positive side of the tube, indicating the decomposition of the salt, the alkali or *soda* of which is collected in the *negative*, and the *sulphuric acid* in the *positive*, side. Reverse the poles, and the colors will also gradually be reversed. In this and analogous experiments, it is found that, whenever a neutral salt is decomposed by electricity, the oxide or base appears at the cathode, and the acid at the anode. The bases, therefore, in their electrical relations, rank with hydrogen, and are cathions; and the acids with oxygen, and are anions.

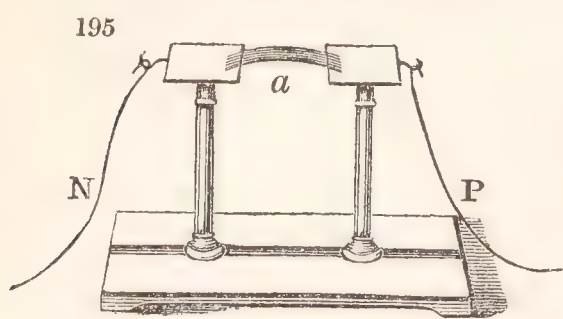


The most difficultly soluble salts may be made to render up their elements in the same way. If, for instance, we substitute for the sulphate of soda in the preceding experiment, a little finely-powdered *sulphate of baryta* moistened with water, baryta will be evolved at the cathode, and there render the liquor green; and sulphuric acid at the anode, rendering it red.

These experiments may be instructively varied as follows:—fill two glasses, connected together by a syphon of large bore, with the blue solution of *sulphate of soda*, and invert in each glass a tube of the same solution, into the upper ends of which platinum wires, terminating in long strips of the same metal, are inserted, as shown in fig. 194; connect these wires with the battery so as to make them the electrodes, and it will presently be remarked, that, notwithstanding they are in separate vessels, the blue liquor will, as before, be rendered green and red; and



if the experiment be continued for a sufficient length of time, the alkali of the salt will have passed from the side P to N, and the acid from N to P. The acid and alkali appear, in this, case to traverse the connecting syphon in opposite directions; hence the inference that, under the influence of electrical attraction, the usual chemical affinities are suspended.



The decomposition of *sulphate of baryta* may be effected in the same way; for this purpose, provide two insulated discs, or shallow cups of platinum (fig. 195), one of which is to be put into communication with the negative, and the other with the positive, end of the pile; place upon each of

these a few grains of finely-powdered (artificial or precipitated) sulphate of baryta, moistened by a drop or two of water, and connect the discs (which should be within half an inch of each other) by some filaments of wet cotton, *a*. In a few minutes *baryta* will be apparent to test-papers at the negative disc, and *sulphuric acid* at the positive.

In some of his experiments on these electrical transferences, Sir H. Davy employed vessels consisting of the substance to be decomposed. Two small cups of *sulphate of lime*, for instance, were filled with water, and united with moist cotton: they were rendered negative and positive by placing one pole of the pile in each cup; the negative cup soon was found to contain a solution of *lime*, and the positive cup free *sulphuric acid*.

If the bent tube, fig. 193, be filled with a dilute solution of sulphate of copper, acetate of lead, or nitrate of silver, the metals will be deposited upon the cathelectrodes, and no hydrogen will escape. In this way, M. Becquerel, by employing low voltaic powers, obtained some beautiful results, and succeeded in imitating many crystallized substances found in nature but not previously produced by art. Such experiments have been further extended and improved, and some new and important chemical results obtained from them, by Dr. Golding Bird. (*Phil. Trans.*, 1838.)

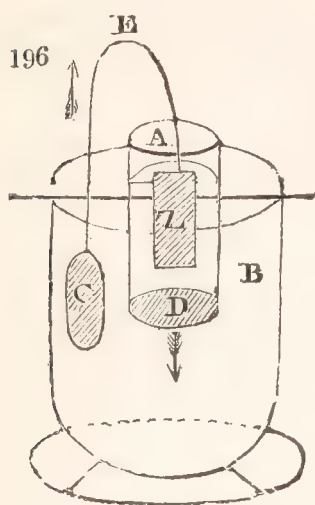
In some of Sir H. Davy's early experiments on the decomposition of water in glass vessels, a considerable quantity of acid and alkaline matter was elicited, which was traced to the glass: to avoid this source of error, therefore, he electrized water in two vessels of gold, properly connected, thus employing a material which could not furnish impurities to the water: still, however, alkali and acid made their appearance. This evolution of foreign matters, by the electrization of *apparently* pure water, had been observed by others; and their appearance was, by some, referred to a power, supposed to be possessed by electricity, of *generating* the matters evolved; it was even imagined that water might possibly be a simple or elementary body, capable of forming an acid in union with positive electricity, and an alkali with negative electricity. In reviewing these and other opinions, it occurred to Davy, that the water, although carefully distilled, and apparently pure when examined by common tests, might still contain minute portions of foreign matter, rendered evident by the decomposing power of electricity. He accordingly carefully redistilled the water at a low temperature in silver vessels, and on employing

it, thus redistilled, it was found to afford much less indication of impurity; but, even after all precautions, acid and alkali were sparingly evolved. Of this impurity, part was traced to the accidental contact of the hands with the apparatus used, the perspirable matter leaving traces of common salt; and now, aware of this source of contamination, and carefully avoiding it, there were scarcely any traces of acid or alkali to be observed. These extraneous elements, however, notwithstanding all the precautions, were still perceptible after the process of electrical decomposition had been carried on for a length of time; and the only probable source whence they could be derived was the atmosphere, the elements of which, by uniting chemically with those of water, might give rise to the formation of nitric acid and ammonia. This chemical action or combination, Davy thought, might possibly be brought about by electric agency; accordingly, in addition to all the previous precautions, he now conducted the experiments in the exhausted receiver of a good air-pump, and found that under the careful exclusion of all foreign agents, water was apparently resolved into oxygen and hydrogen only; and, consequently, that there were, at all events, no grounds for supposing that any new forms of matter were *producibile* by the union of electricity with other bodies.

Another important inference was deduced from the above, and similar experiments; it was obvious that electricity overcame the most powerful chemical attractions; might it not, therefore, when properly applied to different bodies, indicate the existence of substances hitherto unsuspected, and even lead to the knowledge of new elements? Proceeding upon such grounds, Sir H. Davy submitted the fixed alkalis, which were considered at that time as elementary bodies, to the agency of the pile, and was fortunate enough in this, his first trial, to obtain from them new elements: at the positive pole oxygen was evolved, but brilliant metallic globules appeared at the negative pole, extremely inflammable, and which were shown to be the bases of those bodies. The names *potassium* and *sodium* were given to these new and singular metals; and by analogically applying these phenomena of the decomposition of the alkalis to that of the *earths*, also then on the list of elements, they likewise afforded evidence of decomposition, and, like the alkalis, were shown to be combinations of peculiar metals with oxygen. Many other discoveries have been the result of this new mode of research, which will be more fully dwelt upon afterwards.

The metallic precipitations above adverted to, as deposited upon the negative electrode, have been resorted to for the purpose of taking impressions or copies of seals, medals, copper-plates, &c., forming what have been termed *Electrotypes*, and a new branch of art has thus arisen, which has been termed *Electro-Metallurgy*. For this purpose, the following modification of the voltaic arrangement may be used. The piece of metal to be copied, suppose an engraved copper-plate or a medal, or an indented impression of a medal in lead, tin, or fusible metal, is connected by a copper wire with a rod or plate of zinc, the wire being soldered at one end to the zinc, and at the other to the medal or plate to be copied, and of any convenient length: a glass open at both ends is then provided, (a lamp-glass sometimes answers the purpose,) and one end is closed either by plaster of Paris, or by tying over it a piece of bladder: it is then suspended within a sufficiently large vessel, filled with a solution of sulphate

of copper, which must be kept saturated during the process, either by adding fresh sulphate of copper, or by putting some crystals of that salt into the saturated solution. The smaller vessel is then filled with dilute



sulphuric acid, (1 of acid to 8 of water,) and suspended within the larger one containing the sulphate of copper, as shown in the annexed diagram; where A represents the acid-holder with its porous diaphragm D; B the vessel of solution of sulphate of copper; C the plate upon which the precipitation of copper is intended to take place, and which is connected by the wire E with the zinc plate Z. The darts show the direction of the electric current generated by Z, and transmitted through the diaphragm to C, where the copper is gradually precipitated in a tough metallic layer. When the deposited copper

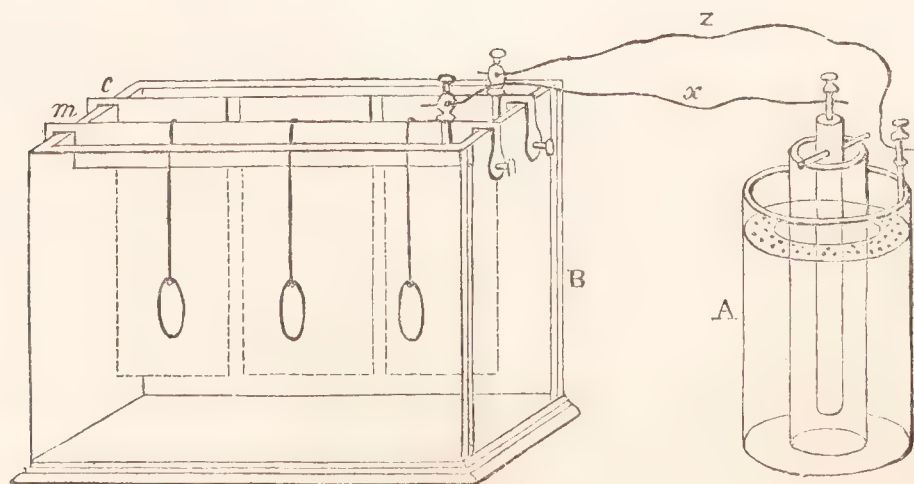
upon C has acquired sufficient thickness, which will generally be in twenty-four hours, it may be removed by carefully loosening its edge with a knife, and then pulling it gently off the mould. Several moulds may, if requisite, be connected with the zinc plate.

These metallic precipitations have been beautifully applied to the purpose of gilding and silvering in general, and electrotype processes have now to a great extent superseded the old methods of plating: the metallic solutions best adapted for these purposes will be noticed under the respective metals.

In copying seals, wax and plaster casts, and other nonconducting substances, it is necessary to cover them with a conductor: for this purpose Mr. Robert Murray ingeniously devised the application of plumbago. (*Trans. Soc. Arts.*) A deposition of silver and other metals may also be, in many cases, conveniently effected by dipping the substances into a solution of phosphorus in sulphuret of carbon, and then into a proper metallic solution: the phosphorus reduces a film of metal upon the surface, which is now adapted to receive the electric deposition.

Instead of the simple form of apparatus above represented, a separate source of electricity is now generally used, consisting of one or more of Daniell's or Smee's arrangements, and a *working cell* containing the moulds and proper metallic plates and solutions, placed either vertically or horizontally, as is found convenient. Fig. 197 represents an arrangement of this kind. A is a constant battery; B the decomposition cell;

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m a metal rod for supporting the moulds; *c* a similar rod for supporting the copper plates; the wire *x* connects the moulds *m* with the zinc of the battery, the wire *z* connects the copper plates *c* with the copper of the battery. The cell B contains a mixture of *one* part sulphuric acid, *two* parts saturated solution of sulphate of copper, and *six* or *eight* or *more* parts of water, according to circumstances. Copper is *consumed* from the plates *c* by union with the oxygen liberated there, and carried over and *deposited* on the moulds *m*; and this consumption and deposition are exactly equal; so that, so far as this action is concerned, the solution is in the same condition at the *end* as at the *beginning* of the experiment. Had platinum plates been used instead of copper *c*, the deposition would have occurred at the expense of the *solution*, which would soon have been exhausted; and, in that case, one generating cell would not have done the work. It will be seen in the arrangement before us, that the cell B offers very little resistance to the current, for the affinity of the oxygen for the copper is of the same character, though less in degree, and exerted in the same direction as the affinity of the oxygen for the zinc in the generating cell A. (WALKER, *Electricity and Magnetism*, II., 368.)

The details of these operations are given in several works expressly upon the subject by Walker, Smee, and others.

In all *primary* electro-chemical decompositions, the elements of compounds are, as we have already shown, evolved with uniform phenomena either at the anode or cathode of the electrolyte; hence their division into *electro-negative* and *electro-positive* bodies, or, into *anions* and *cations*. But it frequently happens that the evolution of a substance at the electrode is a secondary effect; *sulphur*, for instance, in the decomposition of sulphuric acid, is evolved at the cathode or negative pole, not by *direct* electrolysis, but in consequence of the action of the nascent hydrogen; and whenever sulphur is obtained by primary electrolytic action from a compound containing it, it is evolved at the anode, or positive pole; hence, in classifying the elements according to their electrical relations, this distinction must be observed. It is also necessary to guard against the combination of the substance evolved (or *ion*), with the electrode; hence the advantage of platinum electrodes, that metal being acted upon by very few of them.

The following table of *simple and compound ions* has been drawn up by Faraday:

ANIONS.

Oxygen	Cyanogen	Phosphoric acid	Citric acid
Chlorine	Sulphuric acid	Carbonic acid	Oxalic acid
Iodine	Selenic acid	Boracic acid	Sulphur
Bromine	Nitric acid	Acetic acid	Selenium
Fluorine	Chloric acid	Tartaric acid	Sulphocyanogen.

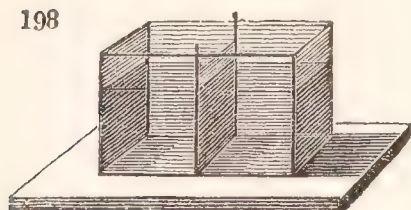
CATIONS.

Hydrogen	Tin	Mercury	Strontia
Potassium	Lead	Silver	Lime
Sodium	Iron	Platinum	Magnesia
Lithium	Copper	Gold	Alumina
Barium	Cadmium	—	Protoxides generally
Strontium	Cerium	Ammonia	Quinia
Calcium	Cobalt	Potassa	Cinchonia
Magnesium	Nickel	Soda	Morphia
Manganese	Antimony	Lithia	Vegeto-alkalis gene-
Zinc	Bismuth	Baryta	rally.

Analogy leads us to presume that all simple bodies are *ions*; but this has not yet been experimentally proved in regard to carbon, phosphorus, nitrogen, silicon, boron, and aluminum: several compound bodies are in the same uncertainty.

For the purpose of popularly illustrating the general phenomena of the electro-chemical decomposition of aqueous saline solutions, and for

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some other experiments of decomposition, the annexed form of apparatus (fig. 198), will be found useful. It is a flat cell of glass, about five or six inches long, and an inch broad, and may be

divided into two parts, by the insertion of the temporary diaphragm *a*, which is a small frame of cane with muslin stretched over it. When this is in its place, a separate electrode may be introduced on each side of it: they may most conveniently consist of two pieces of thin platinum, about four inches long and half an inch broad.

To show the evolution of *chlorine* at the anode (or positive pole), fill the glass cell with a solution of chloride of sodium in water, colored blue by the addition of a few drops of a sulphuric solution of indigo; then introduce the electrodes, and in a few minutes the *positive* or *anodic* division will begin to lose color, and at length become colorless, in consequence of the evolution of chlorine derived from the salt: here the presence of *chlorine* is rendered evident by its *bleaching power*, which destroys the blue of the indigo*.

The presence of uncombined *iodine* is announced by its property of striking a deep blue color with a solution of starch. To demonstrate its electro-polarity, therefore, fill the cell with a very weak solution of *starch* to which a little iodide of potassium has been added; then electrize as before, and the *iodine* will show itself at the *anode* (or positive side) by a beautiful *blue* color.

The presence of *bromine*, in the case of the decomposition of a solution of bromide of potassium, is announced in the same way by the yellow color which it gives with the starch. The evolution of *fluorine*, as an anion, may be shewn by its action upon glass as evolved in the electrolysis of a solution of fluoride of potassium.

The electro-positive bodies, or *cations*, on the other hand, are evolved from their combinations with the anions, at the *cathode* (or negative pole), as is seen in the elimination of hydrogen, by the electrolysis of dilute hydrochloric acid, and of the metals in the instances of metallic precipitation already cited: so that when the metals are the cathelectrodes, they are

* In the year 1820, I suggested the possibility of applying these electro-chemical effects to the art of calico-printing, and showed that by bringing a small disc or figure of platinum rendered electro-positive, upon a piece of colored calico imbued with solution of salt, and stretched over an electro-negative surface, white spots or patterns might be produced in consequence of the action of the evolved chlorine; and

that by reversing the electric state of the pattern, the alkali evolved would produce variously colored patterns upon grounds properly prepared for the purpose. A patent has been taken out by Mr. Bagg, for a similar application of electricity, in which he proposes to produce various colors by the application of patterns formed of plates of various metals and alloys acting upon different saline solutions.

rendered virtually attractive of each other, and of the cations or electro-positive bodies in general: thus, under such circumstances, alkalis, earths, and oxides will be separated upon them; but the same cause which thus renders them apparently attractive of these bodies, renders them as it were repulsive of the anions or electro-negatives, among which are the bodies chiefly characterized by their corrosive and solvent action upon them. A piece of iron, for instance, forming the cathelectrode, (rendered *electro-negative*,) will remain bright and clean in water, which, under ordinary circumstances of immersion, would rust and corrode it; but if the iron form the anelectrode, (be rendered *electro-positive*,) it then corrodes more rapidly than in plain water; that is, it is then rendered as it were *attractive* of oxygen, acids, and the other solvent agents, of which, in the opposite case, it is virtually repulsive.

These facts led Davy to infer that certain metallic substances which, under ordinary circumstances, are not acted upon by water and acids, might be rendered *active* by communicating to them the *positively* electrical state; and, on the contrary, that such metals as are easily acted upon by the above-mentioned agents, might be rendered *inert* in regard to them, by giving them the *negatively* electrical state. Silver, for instance, is a metal not acted upon by pure water, nor by dilute sulphuric acid. But, if the electrodes consist of two strips of silver, immersed in the acidulated water, while the cathelectrode (or negative pole) remains bright, the anelectrode (or positive) becomes discolored, and a cloud collects about it in the water, which is *oxide of silver*; here, the silver is rendered *attractive* of oxygen, and combines with it.

If, for water, we substitute a weak solution of common salt, or dilute hydrochloric acid, the *negative* silver will still remain bright, but the *positive* becomes incrustated with a white or gray powder, and is soon corroded; this arises from its being rendered *attractive* of the chlorine contained in the salt and in the acid, and *chloride of silver* is formed.

If we substitute for silver any more oxidizable metal, the effects are still more striking, and we then have a better opportunity of observing the non-action at the negative surface, as opposed to the activity of the positive. For instance, for the silver electrodes substitute two polished plates of *iron*, and immerse them into weak sulphuric or hydrochloric acid, or into a solution of salt, liquids which, under ordinary circumstances, act upon and corrode iron; the negative plate, or cathelectrode, will now remain bright, but the positive, or anelectrode, will be oxidized and dissolved.

This experiment may be varied, as follows: Fill the glass cell, fig. 198, with a weak solution of common salt in distilled water, to which a few drops of a solution of ferrocyanide of potassium have been added, and immerse one of the iron plates in each partition; the negative side will remain unchanged, but the production of a deep blue color on the opposite side, will announce the action upon the iron there going on. If we substitute a little infusion or tincture of galls for the ferrocyanide, the solubility of the iron is then shown by a black tint.

The want of action of the cathelectrode (or negative conductor) shown in these experiments, may be more explicitly illustrated by the following: Silver and copper are readily acted upon by *dilute nitric acid*; it dis-

solves them with effervescence; but if plunged into the acid when rendered *electro-negative*, (or forming the cathelectrode,) they *resist* its solvent or oxidizing power. It will be borne in mind that, in all these cases of the apparent protection of oxidizable metals in fluids containing water, *hydrogen* is evolved upon the protected surface, whence it either passes off as a gaseous film, or is ready to produce secondary effects by entering into new combinations.

Such cases of the prevention of chemical action may be further illustrated as follows: Dilute some nitric acid with five or six parts of water, so that it may act very moderately upon a piece of *sheet-copper* immersed into it; in the course of a few minutes the acid will have acquired a slight blue color from the dissolved copper, which may be rendered more striking by dropping a little of it into a solution of *ammonia*, when a deep blue will immediately announce the presence of copper; but if the copper-plate *be united with one of zinc*, and then plunged into the same acid, it will be found not to have been acted on, the zinc only being dissolved.

Again: immerse a polished plate of iron into a glass of water impregnated with carbonic acid, and in a few hours the water will be discolored, and a portion of the iron dissolved, as may be shown by the black color produced on adding the infusion of galls. Now, tie a strip of zinc in close contact with the iron, and immerse the two metals into the water: after the lapse of some days, none of the iron will have been taken up; indeed, it will remain as bright as when first put in.

Sir H. Davy aimed at a very important practical application of these facts, as a means of preventing the corrosion of the copper-sheathing of ships. It was generally believed that sea-water had but little action upon pure and well-rolled copper, and that its occasional rapid corrosion depended upon some impurity of the metal, or imperfection in its manufacture. It was found, however, on immersing pieces of the best and purest copper in sea-water, that it soon became covered with a green powder, and was corroded. Davy referred this action to the mutual attraction of the *positive* copper and the *negative* oxygen or acid contained in the water, and, therefore, endeavoured to prevent it by communicating a *negative energy to the copper*, by attaching to it a more oxidable metal, such as zinc, iron, or tin. (*Phil. Trans.*, 1824 and 1825.)

In experiments upon the small scale, it was found that a piece of *unprotected* copper, immersed in sea-water, was soon covered by a green powder, part of which was dissolved, and part precipitated; but on attaching to it a piece of zinc, and keeping the metal, thus *protected*, under sea-water, it remained bright and untarnished for several weeks: of the facility, therefore, of thus effectually protecting the copper, there could be no doubt: but a point of great importance in reference to the present question was to determine the relative proportion which it was necessary for the *protecting* metal to bear to the *protected**. When the former was zinc or iron, and amounted to from one-fortieth to one-hundred-and-fiftieth of the copper surface, the latter metal under-

* See also, in reference to this subject, the curious inquiries of Professor Daniell respecting the mutual relations of the generating and conducting surfaces in voltaic arrangements. (*Phil. Trans.*, 1838, p. 31.)

went no change or decay; when the zinc was reduced to one two-hundredth and one four-hundredth, there was some perceptible loss; but it is, to a considerable extent, effectual, where it only amounts to one one-thousandth.

As far, therefore, as *protection* was concerned, the above experiments were satisfactory, and seemed to hold out well-founded hopes of being applicable upon the large scale; but when a negative electric power is thus conferred upon the copper, so as to protect it from oxidizing and corroding agencies, it becomes (as above explained,) attractive of the cations or electro-positive bodies; among these are the *earthy substances* contained in sea-water, such as lime, magnesia, and some of their compounds: these, therefore, when the plan was adopted upon a large scale, and a protected vessel sent to sea, were precipitated or deposited upon the copper. Now it seemed, at first, as if this earthy coating would merely act as an additional preservative of the copper; but, unfortunately, the adventitious crust or surface, thus formed, is most favorable to the adhesion of weeds, and of certain marine animals; and these accordingly attached themselves to it so rapidly, and in such abundance, as to render the bottom extremely foul, and to interfere with, and impede the sailing of the vessel. Theory would lead us to expect, that the zinc or iron might be so exactly proportioned to the surface of the copper, as effectually to protect it, without at the same time communicating to it that tendency to attract an earthy crust, which has just been mentioned; but in practice this has been found scarcely attainable.

An important practical application of this galvanic protection, as it has been termed, has been made in the case of the protection of iron by zinc: for this purpose sheets, plates, and other articles and utensils of iron, either wrought or cast, are properly cleansed, and dipped into melted zinc, so as to become coated by the latter metal; the consequence is that the zinc not only serves as a mechanical defence to the iron, but, by its electrical relations, is extremely effective in defending it from oxidization, and as long as only a very small portion of the zinc remains, the iron resists the rusting energy of air and moisture, and even the more powerful attacks of sea-water and other chemical agents; so that this zinced iron is not only applicable to innumerable domestic and economical uses, but has been successfully applied as a sheathing for ships, and is said not to be liable to those objections of over-protected copper, depending upon the adhesion of weeds and barnacles. As a roofing material it has been adopted by Mr. Barry, upon a very extensive scale, in the new palace at Westminster. In the case of what is termed *tin-plate*, we have an instance of the converse electrical agency: the iron is there the protecting, instead of, as in the preceding case, the protected metal: by the contact of tin it is rendered more susceptible of oxidization, and as soon as any part of the surface is abraded and exposed to solvents, or oxidizers, the rusting of the iron progresses vigorously and counteracts even the mechanical defence of the tin coating.

It will be obvious, from the preceding details, that electrolytic action tends to the separation both of proximate and ultimate elements; of the separation of the *proximate* elements of compounds, the decomposition of neutral salts furnishes ample instances, in which a compound acid and a compound base are respectively separated at the anode and cathode:

whether the sub and super salts or *disalts* and *bisalts* are, or are not, decomposed with precisely the same results, has not, perhaps, been accurately determined, but apparently they are: the case, however, is different with respect to binary compounds of the elementary substances; for among them, (with very few exceptions,) the *proto-compounds*, or those consisting of *one atom* or equivalent of an anion, with *one* of a cation, are those only which are directly electrolytic, whilst other binary compounds of the same elements are not so; thus the fused *protochloride*, and *protiodide* of tin are decomposed, but the *perchloride*, and *periodide* are not; these important differences may depend upon conducting power, for no compound which is not, to a greater or less extent, a *conductor*, is susceptible of this decomposition (with the single apparent exception of periodide of mercury, which Mr. Faraday found to insulate whilst solid, but to conduct whilst liquid, and yet was not decomposed).

The cases of *apparent* decomposition opposed to the law just stated are numerous, but they may be referred to *secondary* electrolytic action. When oil of vitriol, for instance, which is a compound of one atom of sulphur, one of hydrogen, and four of oxygen, is subjected to the action of the electric current, sulphur and hydrogen appear at the cathode, and oxygen at the anode; but, as already stated, Faraday has shown that the sulphur is here the result of the action of the *nascent* hydrogen upon the acid, and that in all cases of the true electrolytic decomposition of the sulphurets, the sulphur is evolved at the anode, and hence is properly placed in the above table of ions, amongst the anions. He observes, in reference to these cases, that the final result of the action of the electric current upon substances placed between the electrodes, instead of being simple, may be very complicated: that substances may be decomposed either by the direct action of the electric current, or by the action of bodies which that current evolves. There are also two modes by which in these cases, new compounds may be formed; that is, by the combination of the evolved substances in their nascent states with the matter of the electrode, (of which the formation of oxide of silver, &c., above referred to, is an instance,) or by their combination with substances, which being contained in or associated with the electrolyte, are necessarily present at the anode and cathode. The decomposition of a solution of *ammonia*, in which the nascent oxygen of the decomposed water unites to the hydrogen of the ammonia, and sets *nitrogen* at liberty at the anode; and that of *nitric acid*, in which the nascent hydrogen of its water, reacting upon the acid, produces *nitrous acid* at the cathode, are instances of such *secondary* results. This complexity is further increased by the circumstance that such actions may occur simultaneously, and in variable proportions to each other. When the electrolyte is an aqueous solution, or when it contains water, such secondary results are very frequent; but they are not confined to cases where water is present: Becquerel has shown that they are in many instances applicable to the formation of new compounds, and to the imitation of those which are produced by natural operations. (*Ann. de Chim. et Phys.*, xxxv. 113.)

Previous to Faraday's researches, it was assumed that all compounds were susceptible of electro-chemical decomposition, and more especially

those in which the elements were held together by feeble affinities*; but it is now apparent that conducting power is one essential requisite; and another (probably, at least) a certain atomic relation of the elements to one another; hence a most important application of electrolytic action to the determination of atomic weights. Faraday has thus expressed this law: "There is but one *electrolyte* composed of the same two elementary *ions*; hence, only single electro-chemical equivalents of elementary *ions*, and not multiples, can go to the electrodes." We may infer, therefore, that in the electrolysis of a compound formed of two elementary substances, the elements will be evolved in *single atomic proportionals*; hence the inference, that *water* is to be considered as a *primary* atomic combination of single atoms of hydrogen and oxygen: and hence the application of electrolytic action to the determination of the equivalent number of the elements in doubtful cases.

We may here again advert to the fallacy of assuming that the metallic poles of the voltaic apparatus, or the electrodes, exert an attractive power over the elements of the electrolyte, and to the once common expression, "that certain substances are *attracted* by the negative pole, and others by the positive pole:" the fact is, that no *single* elementary substance, or *ion*, has any tendency to pass to either of them; sulphur, for instance, charcoal, or finely-divided metals diffused through water, are indifferent to the transfer or passage of the electricity. The *poles* or *electrodes* may even be *water* or *air*. Thus, if pure water be carefully poured upon a solution of sulphate of magnesia, the platinum conductors may be so introduced and arranged, as to make the saline solution, the anelectrode (positive), and the water, the cathelectrode (negative); in this case magnesia will be deposited *at the line of contact between the water and the solution*, but none of it will pass across the water to the platinum cathelectrode; and in all cases in which substances have been supposed to travel by mere attraction, a line of compound particles has extended from pole to pole. (FARADAY. 5th Series, § 493, &c.)

It seems proved by Faraday's experiments, that electricity of very feeble tension may sometimes pass through an electrolyte, without effecting its decomposition; and that, in such cases, the decomposition ensues when the conducting power of the electrolyte is improved, or the intensity of the electricity increased. If, for instance, a solution of sulphate of soda be made part of a circuit transmitting electricity of very low intensity, the galvanometer in such a circuit will be deflected, so as to demonstrate the passage of electricity, but no appreciable decomposition of the salt will ensue; on increasing the *intensity* of the current, the deflection of the magnetic needle is not increased, but the acid and alkali of the salt are separated. (FARADAY. 8th Series, § 977.)

* It follows from Faraday's theory, that the more directly bodies are opposed in chemical affinity, the more easily they are separated by electrolytic action, provided other circumstances, such as insolubility, deficient conducting power, proportions, &c., do not interfere, "so that in applying the voltaic battery for the purpose of de-

composing bodies, not yet resolved into forms of matter simpler than their own, it must be remembered, that success may depend not upon the weakness, or failure upon the strength of the affinity by which the elements sought for are held together, but contrariwise."

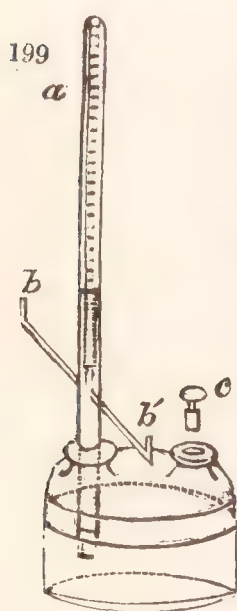
Electrolytes differ in the facility with which they yield up their elements to the influence of the electric current, or in the resistance which they offer to electro-chemical decomposition. (FARADAY, *Phil. Trans.*, 1834, p. 488.) The following bodies are electrolytic in the order in which they are placed, those which are first, being decomposed by the current of lowest intensity :—

Iodide of potassium (solution)	Chloride of lead (fused)
Chloride of silver (fused)	Iodide of lead (fused)
Protochloride of tin (fused)	Hydrochloric acid (solution)
Water acidulated by sulphuric acid.	

That the chemical power is in direct proportion to the absolute quantity of electricity which passes, was an inference drawn by Faraday at an early period of his researches, (*Phil. Trans.*, 1833, p. 53,) and afterwards demonstrated by a series of conclusive experiments, (*Phil. Trans.*, 1834, p. 102,) which led to the development of the *definite nature of electro-chemical decomposition*.

Analysis teaches that *water* is composed of 1 part by weight of hydrogen, and 8 of oxygen, and that *oxide of zinc* consists of 32 of zinc, and 8 of oxygen; now suppose a quantity of electricity set free, or in motion, by the oxidizement of 32 parts of zinc by 9 of water, that quantity will also decompose 9 of water by the platinum electrodes, evolving from it 8 of oxygen and 1 of hydrogen; and the same *quantity* of electricity transmitted successively through fused chloride of silver, and iodide of lead, so as to decompose them, will evolve 36 of chlorine, and 126 of iodine, at the anodes, and 108 of silver and 104 of lead at the cathodes; these numbers are the exact *chemical equivalents* of the respective elements; accordingly, if we place a portion of *water* anywhere in the electric circuit, the quantity of it which is decomposed, or the quantity of oxygen and hydrogen either separate or mixed, which is evolved, furnishes a *measure*, or mode of expressing the quantity of electricity which has passed in a given interval. Faraday has constructed

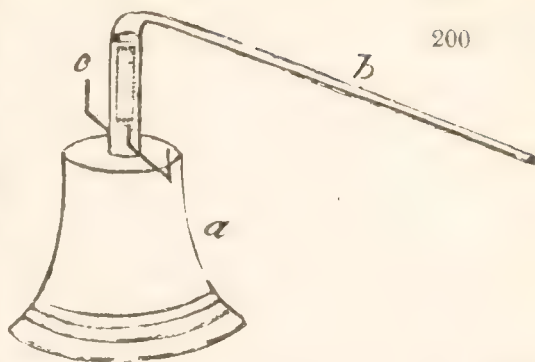
several instruments for this purpose, which he terms *Volta-electrometers* or *Voltameters*: among them the two following will be found most useful. *a* (fig. 199) is a straight tube closed at the upper extremity and graduated; through the sides pass the platinum wires *b b'*, being fused into the glass, and connected with two plates within; the tube is fitted by grinding, into one mouth of a double-necked bottle, one-half or two-thirds full of water (acidulated by sulphuric acid to improve its conducting power). The tube is filled by inclining the bottle, and when an electric current is passed through it, the gases evolved collect in the upper part of the tube, and displace the dilute acid, the stopper *c* being left open: when the graduated part of the tube *a* is filled with the



mixed gases, the electric circuit may be broken by removing the wires connected with *b b*, the stopper *c* replaced, and the meter-tube refilled by properly inclining the instrument: a second measure of the gases is then collected, on re-establishing the circuit, and so on.

Another form of the *voltameter* is the following (fig. 200). It is fixed on a weighted foot *a*, and has the form of a small retort, containing

the two electrodes: the neck *b* is narrow and long enough to deliver gas issuing from it into a graduated jar placed in a small pneumatic trough. The electrode chamber, sealed hermetically at the part inserted into the stand, is 5 inches in length, and 0·6 of an inch in diameter; the neck about nine inches in length, and 0·4 of an inch diameter internally. The



chamber *c* is filled up to the neck with dilute sulphuric acid (sp. gr. 1·3). In both these instruments, the contact of the electrodes with each other within the chamber or tube, is prevented by the interposition of pieces of glass-tube.

I must here refer to Faraday's paper (*Phil. Trans.*, 1834, p. 87, *et seq.*) for some curious and important remarks respecting the influence of different forms of the platinum electrodes in these instruments, and for the experimental proofs, that *variation in the size of the electrodes, causes no variation in the chemical action of a given quantity of electricity upon water*: that their action is uninfluenced by changes in the *intensity*, provided the *quantity of electricity remain the same*: that the quantity of water decomposed is uninfluenced by the *strength* of the dilute sulphuric acid in the volta-electrometer; that, when other solutions are substituted for the acid, the *constancy of the electrolytic action upon water* is not altered; and that, as before stated, when water, and other electrolytes, are subjected to the influence of the electric current, *the quantity decomposed is exactly proportionate to the quantity of electricity which has passed*, notwithstanding all variations in the conditions and circumstances under which they may at the time be placed.

I shall conclude this part of the subject by the following summary of certain points already adverted to respecting *electrolytes, ions, and electro-chemical equivalents*, taken from Faraday's seventh Series of Experimental Researches in Electricity. (*Phil. Trans.*, 1834, p. 111.)

i. A single *ion*, i. e., one not in combination with another, will have no tendency to pass to either of the electrodes, and will be perfectly indifferent to the passing current, unless it be itself a compound of more elementary *ions*, and so subject to actual decomposition. ii. If one *ion* be combined in right proportions with another strongly opposed to it in its ordinary chemical relations, i. e., if an *anion* be combined with a *cation*, then both will travel, the one to the *anode*, the other to the *cathode*, of the decomposing body. iii. If, therefore, an *ion* pass towards one of the electrodes, another *ion* must also be passing simultaneously to the other electrode, although, from secondary action, it may not make its appearance. iv. A body decomposable directly by the electric current, i. e., an *electrolyte*, must consist of two *ions*, and must also render them up during the act of decomposition. v. There is but one *electrolyte* composed of the same two elementary *ions*; at least such appears to be the fact, dependent upon a law, that *only single electro-chemical equivalents of elementary ions can go to the electrodes, and not multiples*. vi. A body not decomposable when alone, as boracic acid, is not directly decomposable by the electric current when in combination. It may act as an *ion*, going wholly to the *anode* or *cathode*, but does not yield up its elements, except

occasionally by a secondary action. Perhaps it is superfluous to point out that this proposition has *no relation* to such cases as that of water, which, by the presence of other bodies, is rendered a better conductor of electricity, and *therefore* is more freely decomposed. vii. The nature of the substance of which the electrode is formed, provided it be a conductor, causes no difference in the electro-decomposition, either in kind or degree; but it seriously influences, by secondary action, the state in which the *ions* finally appear. Advantage may be taken of this principle in combining and collecting such *ions* as, if evolved in their free state, would be unmanageable*. viii. A substance which, being used as the electrode, can combine altogether with the *ion* evolved against it, is also an *ion*, and combines in such cases, in the quantity represented by its *electro-chemical equivalent*. All the experiments agree with this view; and it seems, at present, to result as a necessary consequence. Whether, in the secondary actions that take place, where the *ion* acts, not upon the matter of the electrode, but on that which is around it in the liquid, the same consequence follows, will require more extended investigation to determine. ix. Compound *ions* are not necessarily composed of electro-chemical equivalents of simple *ions*. For instance, sulphuric acid, boracic acid, phosphoric acid, are *ions*, but not *electrolytes*, i. e., not composed of electro-chemical equivalents of simple *ions*. x. Electro-chemical equivalents are always consistent; i. e. the same number which represents the equivalent of a substance A when it is separating from a substance B, will also represent A when separating from a third substance C. Thus, 8 is the electro-chemical equivalent of oxygen, whether separating from hydrogen, or tin, or lead; and 104 is the electro-chemical equivalent of lead, whether separating from oxygen, or chlorine, or iodine. xi. Electro-chemical equivalents coincide, and are the same, with ordinary chemical equivalents.

§ 13. SOURCE OF VOLTAIC ELECTRICITY, AND THEORY OF THE PILE.

THE electrical equilibrium is so easily disturbed, or, in other words, there are so many causes of electrical excitation, and tending to the production of electrical currents, that it becomes difficult entirely to separate them and distinctly to refer to each its due effects: Volta attributed the electricity of the pile to the mere *contact* of the different metals, and regarded the interposed solutions as imperfect conductors, admitting the transfer of electricity when the circuit was completed; and when incomplete, throwing the whole, by induction, into an electro-polar state. This explanation was adopted with some modifications by Sir H. Davy, (*Phil. Trans.*, 1807,) who seems to have considered the electric state of the pile partly as the consequence of the contact of the opposed metals, and partly of the chemical action of the liquid in the cells; and he concluded, from experiments upon the contact of acids with alkalis and metals,

* It will often happen that the electrodes used may be of such a nature as, with the fluid in which they are immersed, to produce an electric current, either according with or opposing that of the voltaic arrangement used, and in this way, or by direct chemical action, may sadly disturb the results. Still, in the midst of all these confusing effects, the electric current, which actually passes in any direction through the decomposing body, will produce its own definite electrolytic action.

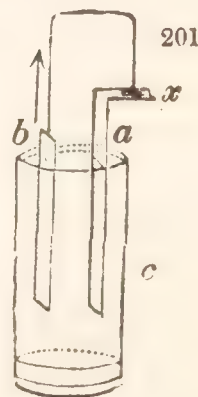
that they became negative and positive in respect to each other*; summing up the whole in the statement, that “Chemical and electrical attractions are produced by the same cause, acting in one case on *particles*, in the other on *masses* of matter, and that the same property, under different modifications, is the cause of all the phenomena exhibited by different voltaic combinations.” (*Phil. Trans.*, 1826, p. 389.)

Others have referred the electricity of the pile exclusively to chemical action: and Dr. Wollaston not only adopted this opinion, (*Phil. Trans.*, 1801,) but attributed the activity of the common electrical machine to the oxidizement of the amalgam: this view was opposed by Davy, who, contrary to Dr. Wollaston’s experiments, found the electric machine active in atmospheres of hydrogen and of carbonic acid, and in the latter more so than in atmospheric air, probably on account of its greater density.

The phenomena of De Luc’s column were considered by some as ample proof of the correctness of the “theory of contact,” while others ascribed its electricity to the chemical action of the moisture hygrometrically retained by the paper; but this and similar arrangements seem to require more minute and accurate examination before satisfactory conclusions can be drawn respecting them.

Faraday, in the 16th and 17th Series of his Researches, (*Phil. Trans.*, 1840,) has ably and impartially discussed the respective claims of the contact and chemical theory, and gives his decided adherence to the latter: contending with De la Rive that there is no current of electricity in the Voltaic pile that is not dependent upon and conjoined with a complete chemical effect; and with Roget, that if there could exist a power having the property ascribed to it by the contact-hypothesis of Volta, namely, that of giving a continued impulse to a fluid in one constant direction without being exhausted by its own action, it would differ essentially from all other powers in nature, and involve suppositions against the truth of which the probabilities are all but infinite. It must, indeed, be allowed, that, independent of all considerations arising out of the unknown nature and cause of electrical currents, both experiment and analogy are strongly against the notion of mere contact as their source.

That electricity is produced in voltaic arrangements, *independent of contact*, and apparently by *chemical action only*, had been satisfactorily shown by Faraday, in 1834, for he found that a single pair of plates, so arranged as to avoid metallic contact and every other source of electricity except chemical action, produced a current which not only deflected a galvanometer, but decomposed iodide of potassium. The following was the form of his experiment. A plate of zinc, about eight inches long and half an inch wide, *a* (fig. 201), was cleaned and bent in the middle to a right angle. A plate of platinum, about three inches long and half an inch wide, *b*, was fastened to a platinum wire, and the latter bent as in the figure. These two pieces of metal were arranged together



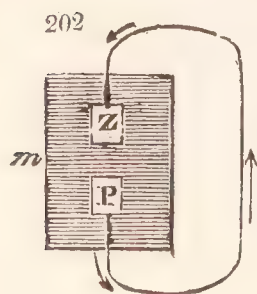
* When two metals, or other substances, are brought into contact, and especially when filings of one metal are sifted upon the surface of another, exceedingly feeble *electricity of tension* may be shown by a

very delicate electrometer; but in these cases, and also when solid *acids* and *alkalis* are used, *friction*, change of temperature, and even chemical action, cannot, as already observed, always be avoided.

as delineated, but as yet without the vessel *c*, and its contents, which consisted of dilute sulphuric acid mingled with a little nitric acid. At *x* a piece of folded bibulous paper, moistened in a solution of iodide of potassium, was placed on the zinc, and was pressed upon by the end of the platinum wire. When under these circumstances the plates were dipped into the acid of the vessel *c*, there was an immediate effect at *x*, the iodide being decomposed, and iodine appearing at the *anode*, i.e., against the end of the platinum wire. As long as the lower ends of the plates remained in the acid, the electric current continued, and the decomposition proceeded at *x*. On removing the end of the wire from place to place on the paper, the effect was evidently very powerful; and on placing a piece of turmeric paper between the white paper and the zinc, both papers being moistened with the solution of iodide of potassium, alkali was evolved at the *cathode* against the zinc, in proportion to the evolution of the iodine at the *anode*. Hence the decomposition was perfectly polar, and decidedly dependent upon a current of electricity passing from the zinc through the acid to the platinum in the vessel *c*, and back from the platinum through the iodic solution to the zinc at the paper *x*. That the decomposition at *x* was a true electrolytic action, due to a current determined by the state of things in the vessel *c*, and not dependent upon any mere direct chemical action of the zinc and platinum on the iodide, or even any *current* which the solution of iodide might by its action on those metals tend to form at *x*, was shown, in the first place, by removing the vessel *c* and its acid from the plates, when all decomposition at *x* ceased, and in the next by connecting the metals, either in or out of the acid, together, when decomposition of the iodide at *x* occurred, but in a *reverse order*; for now alkali appeared against the end of the platinum wire, and the iodine passed to the zinc, the current being the contrary of what it was in the former instance, and produced directly by the difference of action of the solution in the paper on the two metals. The iodine of course combined with the zinc. (*Phil. Trans.*, 1834, p. 426.)

In his 17th series of experiments (*Phil. Trans.*, 1840,) Faraday has given a copious table of similar Voltaic circles. So far, therefore, the evidence of the current of electricity *independent of metallic contact* is complete. It is now to be shown how *chemical action* becomes the source of the electricity in the voltaic battery, and for this purpose I shall insert the following illustrations, for which I am indebted to Mr. Faraday.

Let *z* (fig. 202) represent a piece of pure zinc*, and *p* a piece of platinum, both immersed in dilute sulphuric acid; if they do not touch each other, scarcely any action will take place on the zinc, and none on the other metal; but if they touch, or if they are connected by a long wire of zinc or platinum, as represented in the figure, then action takes place; oxygen from the water combines with the zinc, and forms an oxide, which dissolves; and the equivalent



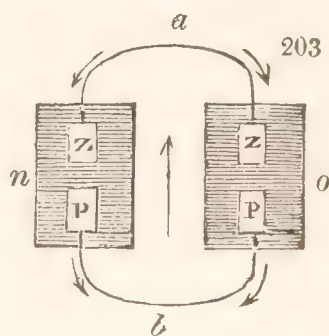
* The impurities in common zinc seem to be the cause of the rapid action exerted upon it by diluted sulphuric acid, which oxidizes it with the evolution of hydrogen. Pure zinc, on the contrary, or, as Mr. Sturgeon has shown, zinc which is super-

ficially amalgamated with mercury, is not, as has already been stated, so acted on, and hence the advantage of using it in cases where the *ordinary* and the *voltaic* action require to be separately observed.

of hydrogen is evolved, and appears against the platinum; whilst the connecting wire exhibits all those characters which show that a current of electricity is passing through it. The *direction* of this current is essentially connected with the chemical action on the zinc, and the evolution of hydrogen on the platinum, and may, at any time, be identified by comparing it with the electricity of the common machine. If the prime conductor and rubber of a machine be connected by a wire, the electricity is said, by a conventional expression, to be passing *from* the conductor through the wire *to* the rubber; and, admitting that standard of reference, it is found in the experiment just described, that the current of electricity produced is from *P* through the wire to *Z*. There are many other solutions, which, if used between the metals *Z* and *P*, will cause a similar effect when the latter are connected by the wire, but the current is *always* in the same direction, and it is also always the zinc which enters into combination. Thus a solution of hydriodic acid, or of the iodide of potassium, will cause iodine to combine with the zinc, hydrogen will appear at the platinum, and a current of electricity will exist in the wire, but of weaker power than before.

In producing this effect, there are two circumstances which seem to be essential, namely, the immersion of the zinc and platinum in the solution, and the metallic contact of the metals, either directly, or by means of the wire: if the contact be broken the current is stopped, and the action on the zinc ceases; or if the metals be taken out of the solution, the action on the zinc of necessity ceases, and again the current is stopped. Hence it became a question for many years, which, though much argued and experimented upon, has only recently been decided, whether it was the chemical action on the solution, or the contact of the metals, which was the real cause of the electric current, and other concomitant effects.

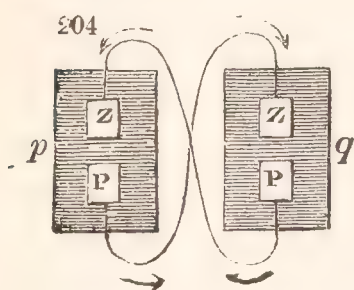
But now consider fig. 203, and let *n* and *o* be two vessels like to *m* (fig. 202), each containing dilute sulphuric acid and pieces of zinc and platinum, and let the two *Z Z* be connected by a zinc wire, and the two *P P* by a platinum wire: no chemical effects will occur, nor any current of electricity be formed; but the moment a wire of any metal is stretched from *a* to *b*, a current of electricity will run up it, dividing right and left, as is shown by the arrows, and oxidation of both zincs will take place, accompanied with the evolution of hydrogen at both platitudes.



Consider this cross-wire as still retained in its place, but the dilute sulphuric acid removed from the vessel *o*, and replaced by a solution of the iodide of potassium. Still the currents will exist, as represented by the arrows: the chemical action will remain unchanged in the vessel *n*; and in the vessel *o*, iodine will combine with the zinc, and hydrogen appear against the platinum. As yet the conditions both of *chemical action* and *metallic contact* exist, the cross-wire from *a* to *b* ensuring the latter; but now remove that wire, and instead of a cessation of action, the following change of effects will take place: the electric current from *b* across to *a* of course no longer exists; that from *a* through the vessel *n* to *b* will be weakened, and the chemical action in *n* much diminished; but the current from *a* through *o* to *b* will be actually inverted, and the

chemical action in *o* will be inverted also, and the iodine will now appear in its free state against the platinum *p*, instead of combining with the zinc, and the hydrogen will appear at the opposite side.

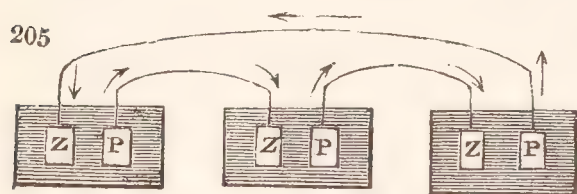
Hence, not only is it proved that metallic contact is not necessary, and that chemical action is the cause of the phenomena, but also that two distinct chemical actions may be opposed, and the weaker made to yield to the stronger; and thus, electro-chemical *excitation* and electro-chemical *decomposition* are shown existing together in the simplest manner as *cause* and *effect*.



If two distinct chemical actions can be thus shown connected together in *opposition* to each other, so also can they be shown with equal simplicity associated in accordance with each other; and in this consists the *principle of the voltaic pile or trough*: for consider again the tendencies and directions of the two sets of forces, as indicated by the arrows, in the vessels *n* and *o*, fig. 203, and then divide the

connecting wire at *a* and *b*, connect the right-hand end of *a* with the left-hand end of *b*, and the right-hand end of *b* with the left-hand end of *a*, as in fig. 204, and then it will be seen by simple inspection, (what is found as a matter of fact,) that the forces in *p* and *q* aid and exalt each other, instead of exerting a mutual opposing action.

Fig. 205 is the representation of three such actions combined, and



with 300 or 3000 the principle is the same; the pull on the general current being, as it were, aided by every recurrence of the zinc, and its vigor and intensity exalted.

In reflecting upon the source of electricity in voltaic arrangements, and upon the definite nature of its action, as shown in the experiments above quoted, it becomes almost impossible to doubt the *identity* of the cause of chemical and electrical phenomena, and from an attentive consideration of the manner in which the elements of electrolytes are evolved at the anode and cathode, the insufficiency of that theory which referred the phenomena of their decomposition to the mere *attractive powers of the poles* must be quite obvious: they must certainly be attributed to some specific action of the electric current, pervading the whole of its course through the electrolyte; and if we regard it, with Faraday, (*Phil. Trans.*, 1833, p. 696,) as “an axis of power having contrary forces, exactly equal in amount in contrary directions,” we may also assume that electro-chemical decomposition is produced “by an internal corpuscular action exerted according to the direction of the electric current, and that it is due to a force, either superadded to, or giving direction to the ordinary chemical affinity of the bodies present. The body under decomposition may be considered as a mass of acting particles, all those which are included in the course of the electric current contributing to the final effect; and it is because the ordinary chemical affinity is relieved, weakened, or partly neutralized by the influence of the electric current, in one direction, parallel to the course of the latter, and strengthened or added to in the opposite direction, that the combining particles have a tendency to pass in opposite courses.”

§ 14. IDENTITY OF VOLTAIC AND COMMON ELECTRICITY.

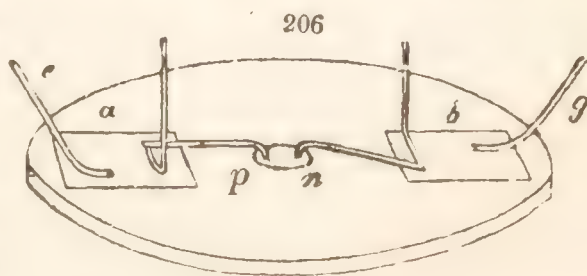
THE phenomena of the voltaic pile are, upon a superficial view, so different from those of common electricity, as frequently to have been referred to a distinct cause, and although they were found, when more accurately compared, to present many analogies, it was long before they were allowed to be absolutely identical. Faraday was led to revise the experiments already made in reference to this question, and to devise many new illustrations of it: his results are published in the third Series of his Experimental Researches. (*Phil. Trans.*, 1833, p. 23.) He has arranged electrical phenomena, for the purpose of this comparison, under two heads; namely, those connected with electricity of *tension*, and those connected with electricity of *motion*; the former includes attractions and repulsions at sensible distances: the latter (or the effects of electrical *currents*) includes the production of heat, magnetism, chemical decomposition, physiological phenomena, and the spark.

1. The *attractions and repulsions* produced by voltaic electricity, and so far identifying it with that of the common electrical machine, have been above described.

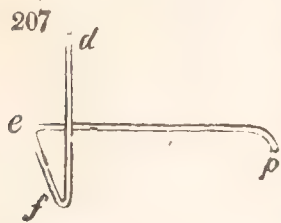
The escape of common electricity through rarefied air, is another effect due to its tension. On endeavouring to discharge a voltaic battery of 140 pairs of plates by approximated pointed wires, either with intervening air, or in a vacuum, no indications of a current, either by magnetical or chemical action, were obtained; but upon *heating* the air between the points by the flame of a spirit-lamp, the current passed, so as to decompose iodide of potassium, and deflect the galvanometer in another part of the circuit. The arc of flame between charcoal points in air and in a vacuum is a similar phenomenon. Another proof of the tension of the electricity of the pile, is the charge of a Leyden battery, which may be effected by De Luc's column and by the voltaic battery.

2. As concerns *electricity in motion*, that of the voltaic apparatus produces heat, magnetism, chemical decomposition, shocks, and sparks, and in these respects the analogies with common electricity are complete. Of the *heating power* of common electricity, instances have been already given, both as relates to the common spark and to that of the Leyden jar or battery. For delicate experiments upon this subject, Mr. Harris's sensible electrometer may be used. (*Phil. Trans.*, 1827, p. 17.) The production of *magnetism* by common electricity has also been satisfactorily proved, by the deflection of the galvanometer, and by the simple experiment of affixing a steel needle at right angles to a wire through which the Leyden jar or battery is discharged, and which receives permanent magnetism.

The power of common electricity to effect *polar chemical decomposition*, was first shown by Dr. Wollaston, (*Phil. Trans.*, 1801, p. 427,) and has been amply verified by Faraday. Upon a glass plate (fig. 206) placed over, but raised above, a piece of white paper so that shadows may not interfere, put two pieces of tin-foil *a b*; connect one



of them by an insulated wire *c* with the positive conductor of the machine, and the other by the wire *g* with the ground, or with the negative conductor: provide two pieces of fine platinum wire, bent as in fig. 207, so that the part *d f* shall be nearly upright, whilst the whole is resting on the three bearing points *p e f*: place these as in fig.



206; the points *p n* then become the decomposing poles. Place a large drop of *hydrochloric acid*, rendered blue by sulphate of indigo, so that *p* and *n* may be immersed in it at opposite sides, then send a current of electricity through it from a machine in good action,

and *chlorine*, shown by its bleaching effects, will be evolved at *p*. This experiment is the counterpart of that with voltaic electricity already described. Place a drop of solution of *iodide of potassium* mixed with starch between the poles, and the current will evolve *iodine* at *p*. Put a drop of solution of *sulphate of copper* between the poles, and the current will then cause the precipitation of *copper* at *n**.

In all these experiments the direct passage of *sparks* must be carefully avoided. If *sparks* are passed over moistened litmus-paper, it is reddened; and if over paper moistened by iodide of potassium, iodine is evolved; but these effects must be carefully distinguished from those due to true *electrolytic* action, and must be cautiously avoided when the latter are sought for. The effect just mentioned appears to be due to the formation of *nitric acid* by the combination of the oxygen and nitrogen of the air: the acid so formed, though very small in quantity, is in a high state of concentration, and therefore reddens the litmus-paper and decomposes the iodide. By moistening a very small slip of litmus-paper in a solution of caustic potassa, and then passing a succession of electric sparks over its length in the air, Mr. Faraday gradually neutralized the alkali and ultimately rendered the paper red, and on drying it he found that *nitrate of potassa* had resulted from the operation, and that the paper had become touch-paper. These experiments furnish simple and ready means of illustrating Cavendish's experiment of the formation of nitric acid from atmospheric air; and render it probable that the singular odor produced by the electric discharge, as when the electricity of a powerful machine is suffered to pass off by points, or in a succession of long and rapid sparks through the air, may be derived from the production of that acid†.

* A curious experiment, which has been called *electro-chemical*, consists in tracing lines or devices upon a thin plate of glass covered with lac varnish, with the knob of a positively charged Leyden phial; *positive* electricity is thus communicated to the side touched, and corresponding lines of *negative* electricity are produced by induction, upon the opposite side. If we now suspend the glass plate insulated in the air, and blow upon it a finely-powdered mixture of sulphur and red lead, the *latter* only will adhere to those parts of the plate which are *positively* electrified. If we now blow the same mixture upon the other side of the plate, the *sulphur* alone will adhere to the

parts which are *negatively* electrified. Thus the same lines will be traced upon both sides of the glass plate, but with different coloured powders, the *positive* lines being *red* and the *negative* *yellow*. The cause of this appears to be, that when sulphur and red lead are triturated together, the *former* acquires *positive*, and the *latter* *negative* electricity: hence the respective powders attach themselves to those surfaces which have an electricity *opposed* to their own.

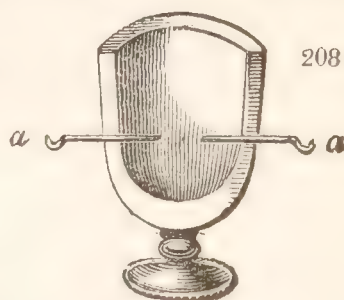
† A similar odor is observed during the decomposition of water by the voltaic current, and has been referred by Schönbein to a peculiar principle called *ozone*.

Though the above experiments amply demonstrate the identity of the decompositions effected by common and voltaic electricity, the true *polar* decomposition of *water* by the former has not hitherto been so effected as to collect an appreciable portion of oxygen and hydrogen, at the positive and negative poles: Faraday's experiments, however, leave no doubt as to the reality of such decomposition. When sparks or shocks are transmitted through water by fine metallic points, streams of gas arise from them*, but they consist of oxygen and hydrogen at each pole, and depend upon some cause, distinct from that which regulates the transference and final place of the evolved bodies, in cases of true electrochemical decomposition.

The *physiological effects* of the common electric current may be considered the same with those of voltaic electricity, account being taken of the *intensity* of the one, and the *duration* of the other.

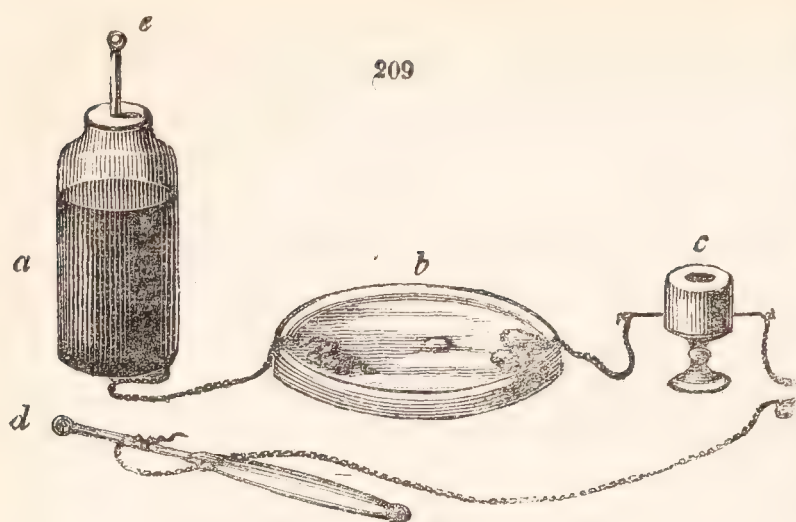
With regard to the *spark*, that from common electricity rivals in brilliancy the splendid light of the voltaic discharge, but it endures for the fraction of an instant only. When the voltaic and the common spark are taken between amalgamated surfaces of metal, at intervals only, and through the same distance of air, the eye can distinguish no difference between them. A curious modification of the spark of a Leyden jar or battery is obtained, by causing the electricity to pass through some distance of water or other imperfect conductor, such as a piece of wet string, so placed as to form a part of the circuit: the spark is then yellowish, flamy, of sensibly longer duration than if the water had not been interposed, and is accompanied by little or no noise; if taken between pieces of charcoal it is extremely luminous and bright upon both surfaces of the charcoal: thus, whilst losing part of its usual character, it, in some degree, approximates to the voltaic spark. The *retardation* which the current of electricity suffers in being thus made to traverse water, is well illustrated by its effect in inflaming gunpowder. In attempting to ignite gunpowder by the discharge of a Leyden jar, unless it is finely powdered and rammed into a small tube or quill, and the discharge of a large jar or battery passed through it by points of iron wire, it it generally thrown about but not exploded. Place

the powder, for instance, in a small ivory mortar, of which fig. 208 is a section, and discharge a moderate-sized Leyden jar through it, so that the spark may pass between the interrupted wires *aa*; in this case the powder will be dispersed, and not ignited. But now repeat the experiment, placing a basin of water in the circuit, so that it may be interrupted by ten or twelve inches of that fluid, and the spark that passes under such circumstances will invariably fire the powder; or, the circuit may be interrupted by a few inches of pack-thread well soaked in water, and the same effect will ensue. Fig. 209 is a representation of the arrangement: *a* is a Leyden jar with a piece of chain touching its exterior coating, and immersed at the other end into the shallow dish of water *b*,



* This experiment was first made by the associated Dutch chemists, Van Troostwijk, and Dieman, in 1789 or earlier; it was repeated by Dr. Pearson in 1797

(NICHOLSON'S *Jour.*, 4to. i.), and afterwards by Dr. Wollaston in 1801. (*Phil. Trans.*)



from the opposite side of which another chain issues, attached to one of the conductors of the mortar *c*; a chain is also attached to the opposite conductor; and the discharge is effected, by bringing the ball of the discharger *d* in contact with the knob of the jar *e*. When the circuit is entirely metallic, the passage of the electricity is apparently too rapid to kindle the powder, but it does so when retarded somewhat in its progress, by being made to traverse the water.

§ 15. ANIMAL ELECTRICITY.

THERE are some remarkable instances of the generation of electricity in living animals, to whom the power seems to be given principally as a means of defence. Of these animals, the *Torpedo* or *Electric ray*, was noticed by the ancient writers on natural history: it inhabits the Mediterranean and North Seas; its weight, when full grown, is about eighteen or twenty pounds. When touched, it communicates a benumbing sensation, and by repeated contacts, gives a series of electric shocks.

The *Gymnotus*, or *Electric eel*, was first described in 1677, by M. Richer, who was commissioned by the French Academy to make some mathematical observations in Cayenne. It is a native of the warmer regions of Africa and America, inhabiting the larger rivers, especially those of Surinam. In Africa it chiefly occurs in the branches of the Senegal. These animals have been anatomically described by John Hunter in the 63rd and 65th volumes of the *Philosophical Transactions*. Their electric organs consist of membranous septa, and are most abundantly supplied by nerves; their too frequent use is succeeded by debility and death. That these organs are not otherwise essential to the animals, is shown by their thriving after they have been removed.

The *Silurus electricus* is less perfectly known: it has been described by Broussonnet under the name of *Trembleur*. (*Histoire de l'Académie Royale des Sciences*, 1782.)

Walsh, Ingenhousz, Cavendish, Sir H. Davy, and Dr. Davy, (*Phil. Trans.*, 1773, 1775, 1776, 1829, and 1832,) have each experimented on this form of electricity, and their joint results leave no doubt as to its identity with common and voltaic electricity. Mr. Faraday, availing himself of a *gymnotus* brought to this country by Mr. Porter, and purchased by the proprietors of the Adelaide Gallery, has more recently instituted new inquiries respecting the electric powers of this extraordinary animal. (*Phil. Trans.*, 1838.)

Humboldt, in his *Tableau Physique des Régions Equatoriales*, &c., has given some curious details respecting the electrical eel which inhabits the rivers and lakes of the low provinces of Venezuela and the Caraccas. It is met with most frequently in the stagnant ponds dispersed at intervals over the plains which extend from the Orinoco to the Apuré. The old road near Urutica has even been abandoned, on account of the danger

experienced in crossing a ford, where the mules were, from the effect of the shocks, often paralysed and drowned. Even the angler is said sometimes to have received a stroke conveyed along his rod and line. These eels are about six feet in length, and occasion a highly painful sensation, more resembling the effect of a blow on the head than the shock of a common electric discharge; a peculiarity referable perhaps to a great quantity of electricity of small intensity. The following particulars given also upon the authority of Humboldt (*Edin. Review*, vol. xvi. p. 250) are too curious to be here omitted.

“The Indians entertain such a dread of the *Gymnotus*, and show so much reluctance to approach it when alive and active, that Humboldt found extreme difficulty in procuring a few to serve as the subjects of experiment. For this express purpose, he stopped some days on his journey across the *Llanos* to the river Apuré, at the small town of Calaboze, in the neighbourhood of which he was informed that they were very numerous. But, though his landlord took the utmost pains to gratify his wish, he was constantly unsuccessful. At last he determined to proceed himself to the spot, and was conducted to a piece of shallow water, stagnant and muddy, but of the heat of 79 degrees, surrounded by a rich vegetation of the great Indian fig-trees and odoriferous sensitive plants. Here he soon witnessed a spectacle of the most novel and extraordinary kind: about thirty horses and mules were quickly collected from the adjacent savannahs, where they run half wild. These the Indians drove into the marsh. The *gymnoti*, roused from their slumbers by the noise and tumult, mount near the surface, and swimming like so many livid water serpents, briskly pursue the intruders, and gliding under their bellies, discharge through them the most violent and repeated shocks. The horses, convulsed and terrified, their mane erect, and their eyes staring with pain and anguish, made unavailing struggles to escape. In less than five minutes, two of them sunk under the water and were drowned. Victory seemed to declare for the electric eels. But their activity now began to relax. Fatigued by such expense of nervous energy, they shot their electric discharges with less frequency and effect. The surviving horses gradually recovered from the shocks, and became more composed and vigorous. In a quarter of an hour the *gymnoti* finally retired from the contest, and in such a state of languor and complete exhaustion, that they were easily dragged on shore by the help of small harpoons fastened to cords.”

The *gymnotus* experimented with by Faraday gave a powerful shock when one hand was placed near each extremity of the fish. By the proper application of conductors it affected the galvanometer, and made a magnet; polar decomposition of iodide of potassium was easily effected by it, with such phenomena as indicated a current passing from the anterior to the posterior parts of the animal; and, lastly, the spark was obtained.

Those who are fond of supposing that electricity is an agent in some of the processes of vitality, have referred, in favor of their hypothesis, to certain other cases of its production by arrangements of different organic substances. If the hind legs of a frog be placed upon a glass plate, and the crural nerve dissected out of one made to communicate with the other, it will be found, upon making occasional contacts with the remaining crural nerve, that the limbs of the animal will be agitated at each contact.

Hence some physiologists suppose that electricity may be concerned in some of the most recondite phenomena of life, and experiments have been made tending to confer some probability on this idea. (See important Memoirs on this subject by Matteucci. *Ann. Ch. et Ph.*, 3 Ser. vi. 201).

“The principle once established, that there may exist in the animal economy a power of determining the developement of electric excitement capable of being transmitted along the nerves; and it being ascertained by numerous and decisive experiments, that the transmission of voltaic electricity along the nerves of even a dead animal is sufficient to produce the most violent muscular action, it became an easy step to refer the origin of muscular motion in the living frame to a similar cause, and to look to the brain, a wonderfully constituted organ, for which no mode of action possessing the least plausibility had ever been devised, as the source of the required electrical power.”

Sir John Herschel, from whom I have quoted the last paragraph, extends his ideas upon this subject in the following note. “If the brain be an electric pile, constantly in action, it may be conceived to discharge itself at regular intervals, when the tension of the electricity developed reaches a certain point, along the nerves which communicate with the heart, and thus to excite the pulsations of that organ. This idea is forcibly suggested by a view of that elegant apparatus, the dry pile of De Luc, in which the successive accumulations of electricity are carried off by a suspended ball, which is kept, by the discharges, in a state of regular pulsation for any length of time. We have witnessed the action of such a pile maintained in this way for whole years, in the study of the above-named eminent philosopher. The same idea of the cause of the pulsation of the heart appears to have occurred to Dr. Arnott, and is mentioned in his useful and excellent book on Physics, to which, however, we are not indebted for the suggestion, it having occurred to us, independently, many years ago.” (*Preliminary Discourse.*)

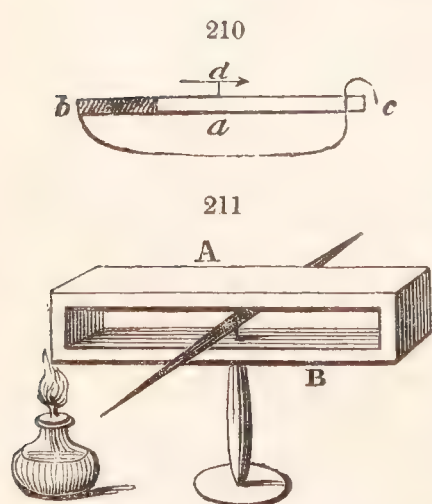
§ 16. THERMO-ELECTRICITY.

IN 1832 Professor Seebeck of Berlin discovered this form of electricity: he found that a bar of antimony, (fig. 210,) *a*, with a piece of brass wire twisted round one end of it *b*, and attached to the other in the form of a loop *c*, when *heated* by the flame of a spirit lamp at the contact of the metals *b*, caused the deflection of a magnetic needle placed at *d*.

A more powerful combination of this kind is obtained by the union of antimony with bismuth: they may be arranged as in fig. 211, so as to form a hollow parallelogram, A represent-

ing the bar of antimony and B the bar of bismuth: on applying heat to one of the junctions by a spirit lamp, a quantitative current of electricity is put into motion through the metals which is immediately indicated by the deflection of a magnetic needle, and this effect is considerably increased if the opposite junction of the metallic bars be at the same time cooled by the application of a piece of ice or of a freezing mixture.

But two metals are not necessary to this effect, for although a plati-

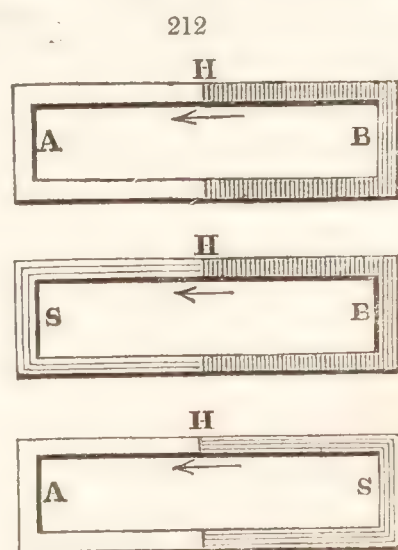


num wire, soldered to the extremes of a galvanometric coil and heated, produces no effect, yet if it be knotted or twisted, a deflection is observed, showing when the heat is applied on the right of the knot, that the direction of the electric current is towards the left: this effect is ascribed to the unequal rate at which the heat travels on the two sides of the obstruction: and again, if the wire be divided, and one end of it be cooled and the other heated, especially if it be of platinum, the needle will deviate when the ends are brought into contact, indicating a current from the hot to the cold surface. If a bar of bismuth be soldered to one end of the galvanometer-wire and a bar of antimony to the other, no effect is produced on bringing the two bars into contact when they are both of the same temperature; but if one of them be either heated or cooled, and then made to touch the other, the flowing of an electric current is immediately indicated.

The term *stereo-electric* has been also applied to this current, implying its production in *solid* bodies independent of a fluid (from $\sigma\tau\epsilon\rho\epsilon\omicron\varsigma$, *solid*) as opposed to the voltaic or *hydro-electric* current.

By forming circuits of the metals taken in pairs, they may be arranged in a series descending from the extreme negative, which is bismuth, to the extreme positive, antimony. Their thermo-electric properties have no correspondence either with their voltaic relations, or powers of conducting heat or electricity; neither do they accord with specific gravity, specific heat, or atomic weights. They are, however, upon the whole, most evident in those metals which are most crystalline in their texture. In some cases, as with zinc and silver, the current increases up to a certain temperature (250°); it then ceases, and on increasing the heat reappears in a contrary direction.

From the indefinite use of the terms negative and positive, in reference to the electric current already above adverted to, and from want of precision in regard to the heated and cooled junctions of the metals, the tables of their thermo-electric relations are often difficultly intelligible. In a compound bar, for instance, of bismuth and antimony, and of bismuth and silver, the direction of the electric current will be from the bismuth to the antimony, and to the silver at the heated junctions. But in a compound bar of silver and antimony, it will, under the same circumstances, be from the silver to the antimony. Fig. 212 represents compound bars or thermo-circles of bismuth and antimony, bismuth and silver, and silver and antimony; and assuming the junctions H to be heated, the current of electricity will pass in the direction of the darts. Under this acceptance of the term, therefore, each metal in the following thermo-electric series may be said to be *positive* to those below, and negative to those above.



THERMO-ELECTRIC SERIES.

Bismuth	Palladium	Lead	Copper	Iron
Mercury	Cobalt	Brass	Silver	Arsenic
Nickel	Manganese	Rhodium	Zinc	Antimony
Platinum	Tin	Gold	Cadmium	

By employing several alternations of each bar, and alternately heating and cooling their junctions, *compound thermo-electric circles* of increased intensity may be obtained.

According to the experiments of Nobili, thermo-electric circuits may be formed with substances of lower conducting powers than the metals. He made small cylinders of porcelain clay, and wrapped round the end of each some cotton steeped in a conducting liquid, which served to place them in direct communication with a galvanometer: one of the ends was reduced to a point, and after heating it to redness by a spirit-lamp, was pressed on the cold extremity of the other cylinder, when a current was established from the hot to the cold part of the arrangement. This effect has, however, been ascribed to the mutual reaction of the two portions of liquid at different temperatures.

All the phenomena of the thermo-electric current show it to depend upon considerable *quantity* opposed to very feeble *intensity*; it is indeed apparently sluggish even in its passage through metals; in that respect therefore directly opposed to common electricity. It is most easily cognizable by the deflection of the magnetic needle; it has been made to produce heat, light, and chemical effects, and to convulse the limb of a frog. (NOBILI, *Bib. Univ.*, xxxvii. 15. BOTTO, *ibid.* xxxiii. 359. WHEATSTONE. *Phil. Mag.* x. 414. WATKINS, *ibid.* xl. 304, 399.)

A beautiful application of a thermo-electrical apparatus has been made by Nobili and Melloni, (*Bull. des Sciences*, 1831,) and employed by the latter in his experiments on radiant heat: they constructed a *thermo-electric pile* of thirty-six pairs of small plates of bismuth and antimony, and attached it to a delicate galvanometer: it was so susceptible of changes of temperature, and, therefore, so delicate a *thermoscope*, as to be affected by the warmth of the hand held at a considerable distance from it: in experiments on radiant heat it is rendered additionally sensible by covering one of its faces with a thin coating of lamp-black. (See the arrangement at p. 112.)

Some theorists have adduced the phenomena of thermo-electricity in support of the contact-theory of the pile, but Faraday's arguments and experiments prove that the two series of phenomena are perfectly distinct; a conclusion also sanctioned by the researches of Becquerel. (*Phil. Trans.*, 1840, p. 122; *Ann. Ch. et Ph.*, xli. 355, xlii. 275.)

Phenomena, in some respects the converse of those which we have called thermo-electric, have been observed by Peltier. When a weak electric current from a single circuit is transmitted through a bar of equal lengths of bismuth and antimony soldered together, from the antimony to the bismuth, heat is evolved at the point of junction, but if in the contrary direction, cold. The effects are appreciable by placing the bulb of a delicate thermometer in a hole at the point of junction; it rises 80° in the first case, and sinks 6° in the second. If the bar be placed on thawing ice, a little water may thus be frozen in the cavity made for the thermometer.

This production of cold by the voltaic current may be demonstrated also in a striking way by the secondary thermo-electric current which it tends to generate. Let a bar of bismuth 4.5 inches long, 0.4 inch square, and a similar bar of antimony, be placed across each other at right angles, and mortice half their thicknesses into each other at the

place where they cross, and solder them together with tin. On connecting two of their ends with a galvanometer, and sending a current through the others, a deflection of the needle will take place on one side from the current generated by the change of temperature; when the direction of the current is reversed, the needle will be deflected in the contrary direction, proving that an opposite change of temperature has taken place from the reversal of the current. That this secondary current is not due to any diversion of the primary current, may be proved by connecting the two ends of the same bar with the galvanometer, and sending the current through the other bar, when no effect will be produced.

These effects of what may, perhaps, be designated as *electro-thermancy*, which we owe to M. Peltier, are the converse of those of thermoelectricity. (DANIELL. *Introd.* § 883.)

§ 17. MAGNETISM.

THERE are certain native oxides of iron which are termed *magnetic iron ores*, and which have the remarkable property of attracting iron filings: when, or by whom this property was originally discovered, is not known; but the Greeks called the iron ore *μαγνητος*, from the name, as it is said, of a shepherd, who first observed it. Pliny describes it under the name of *magnes*, a term said to be derived from Magnesia, a province of Lydia, where this ore abounded.

If a bar of *tempered steel* be rubbed in a certain direction with this native magnet, or *loadstone*, it is itself rendered *permanently magnetic*, and acquires properties similar to those of its source.

There are other means by which magnetism may be temporarily or permanently conferred on iron, and even on other metals; but steel is the only substance (with the exception of nickel) which receives and retains it*: of these sources of magnetism, *electricity* is among the most remarkable, and a new branch of science has arisen out of the phenomena thus presented, called *electro-magnetism*; it is to render the details upon this subject intelligible, that I shall here briefly describe the leading properties of the common magnet, without, however, entering into the theoretical reasonings which have been founded upon them, and which refer to the ultimate *cause* of this important and recondite property†.

The most obvious properties of the magnet are—1, polarity; 2, attraction of iron; 3, attraction and repulsion of another magnet; and, 4, the production of magnetism in iron by induction.

* In making a magnet, a bar of steel is rubbed in *one direction* by a magnet: great care is necessary in observing the direction, and not reversing it, for a powerful magnet may be presently unmade, or rendered unmagnetic, by passing a magnet over it in an opposite direction to that in which its magnetism had originally been conferred. A good abstract of the methods of making artificial magnets, will be found in the *Library of Useful Knowledge*, (Magnetism, p. 41.)

† The compendium of magnetism and electro-magnetism by Dr. Roget, in the *Library of Useful Knowledge*, Professor Cumming's *Manual of Electrodynamics*, the articles on "Magnetism" in the *Encyclopædia Metropolitana*, and the papers of Professor Faraday in the *Phil. Trans.*, are the authorities to which I refer those who wish for information upon the above subjects, and for particulars incompatible with the object of this *Manual*.

1. **POLARITY.** If a slender bar, or needle, of steel rendered magnetic, be poised on a central point, or suspended by a thread so as to have perfectly free motion in a horizontal plane, and to be uninfluenced by neighbouring ferruginous bodies, it will for a time oscillate to and fro, and ultimately settle in a position nearly *north and south*; and if again disturbed, it will vibrate, and again assume the same direction, which, therefore, is called the *magnetic meridian*; this constitutes *magnetic polarity*, and the ends of the needle pointing north and south are usually called its *north and south poles*.

2. **ATTRACTION OF IRON.** On bringing either pole of a magnet near a small piece of iron, it will be attracted; and if iron filings are used, they will cluster about the pole. From the way in which the filings adhere, it appears that in the common magnetic needle, the great attractive force is *near* its extreme ends, or at its *poles*, and that it diminishes towards the centre, at or near which no attraction exists. These attractions are of course *mutual*, that is, the iron attracts the magnet, and *vice versa*.

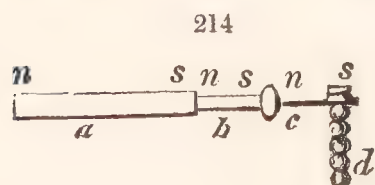
3. **ATTRACTION AND REPULSION OF ANOTHER MAGNET.** If we bring the pole of another magnet near that which is poised, we shall find that if the two *similar* poles be presented to each other, they exhibit a mutual *repulsion*; but that the *dissimilar* poles mutually *attract* each other; here, therefore, we observe an analogy between magnetism and electricity, inasmuch as *between similar powers there is repulsion, and between dissimilar powers, attraction*.

4. **MAGNETIC INDUCTION.** If a bar of iron be brought near a magnet, the iron acquires temporary, or *induced magnetism*; and here again

an analogy to electric induction will be observed. Let *a*, fig. 213, represent a bar magnet, and *b* a bar of unmagnetic and soft

iron, brought to within a short distance of *s*, the south pole of *a*: it will then be found, that whilst in this situation, *b* is a magnet, the poles of which, *n' s'*, are opposed to those of *a*, and consequently attraction subsists between *s* and *n'*; and if a second piece of soft iron, *c*, be placed near *b*, it will also become polar, *n''* being its north, and *s''* its south pole, consequently *s'* and *n''* will attract each other; on withdrawing *a* all magnetic properties in *b* and *c* immediately vanish.

The experiment may be modified, as shown in fig. 214, where *a* is the magnet, *b* a short bar of iron, *c* an iron key, and *d* several iron bullets;



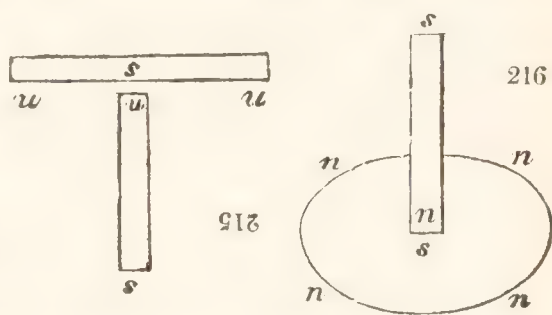
the magnetism in *b c* and *d* is here *induced* by *a*; the respective north and south poles are produced and attracted as before, and each bullet acquires a similar polarity by which they are mutually held together; if *a* be now carefully withdrawn to within a very short distance of *b*, *b c* and *d* will still retain their induced magnetism: but on removing *a* to a greater distance, *b c* and *d* will drop asunder, and all magnetism disappear. When, therefore, a cluster of iron-filings is held by the pole of a magnet, each particle of iron is polar, and the whole is an analogous result of induction.

It has been observed that when a magnet is acting upon a piece of

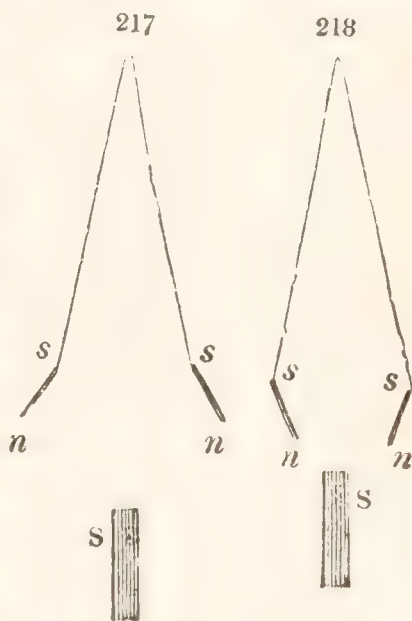
soft iron by induction, as in the case of *a* and *b*, fig. 213, the power or intensity of the magnetism in *a* suffers an increase, and its poles, whilst under induction, have a greater attractive power, and will sustain a greater weight than when that influence is removed.

The intensity of magnetic power developed by induction in an iron bar, is inversely as the distance of the inducing pole from the adjacent end of the bar on which it acts; and the intensity of magnetism induced on the remote end of the bar is, with the same inductive power acting on the nearer end, inversely as the length of the bar. (HARRIS. (*Trans. R. S. Edin.*, 1829.)

When a magnet, instead of being applied as in fig. 213, to the *end* of an iron bar, is applied to its *centre* (fig. 215), both the extremities assume, by induction, a magnetic state *similar* to that of the pole of the inducing magnet, and the centre, an *opposite* state; and if the north pole of a magnet be applied to the *centre* of a circular disc of iron, so that its axis may be perpendicular to it, the plate will have a *central south pole*, and every part of the *circumference* will acquire the properties of a weak *north pole*, as in fig. 216.



The following experiment illustrates the phenomena of induction and of magnetic attraction and repulsion. Attach two short pieces of iron-wire to a thread, and suspend them opposite to each other as in fig. 217. Then bring the pole of the magnet, *s*, slowly towards them; the wires will gradually *diverge* because they become magnetic by induction, and their north poles *nn*, and south poles *ss*, are thus rendered similarly magnetic; but, on advancing the pole of the magnet nearer to the wires, as in fig. 218, its attractive power overcomes the repulsion that exists between the ends *nn*, and they are consequently *drawn towards s*, while the repulsion between *ss* is increased. It is upon this principle that the filaments of polar iron-filings adhering to the pole of a strong magnet, diverge, or are repelled by each other.



All the magnetic properties induced in soft iron cease when it is heated to bright redness; so that if we heat the whole of a small iron bar up to that point, and then bring it near a magnetic needle, it will not affect it; as soon as it is cooled down to a common red heat, the magnetism gradually returns, and is stronger than in the cold iron: but there is one particular period during cooling, between the white and red heat, at which the induced polarity is inverted; or in which the iron attracts the needle the contrary way to what it does when it is cold. (BARLOW, *Phil. Trans.*, 1822, p. 118.) We also find that the permanent magnetism of a steel needle is diminished by a moderate heat, and that a red heat totally destroys it. Mr. Faraday found the induced magnetism of nickel to be destroyed by a heat below redness, and conceives it probable

that the unmagnetic metals are, at *common temperatures*, in the same relation to magnetism as iron at a *bright red heat*, and that at some very low temperature they would exhibit a similar relation to magnetism with that belonging to iron at common temperatures. (In reference to the influence of *temperature* upon magnetism, see a paper by Mr. Christie. *Phil. Trans.*, 1825.)

It is obvious, from the position assumed by the magnetic needle when freely moving in an horizontal plane, that there is some attractive force in the earth, which causes it to assume a constant direction, and that what we have termed the north pole of the magnet, is attracted towards the north pole of the earth, and its south pole by the south pole of the earth; and hence it is inferred, according to the above stated law of magnetic attraction, that the poles of the earth are in an opposite magnetic state to those of the needle.

But the earth has also a further influence upon an artificial magnet, which is only rendered evident when it is so suspended as to move freely in every direction. Under these circumstances, and in our latitudes, the *north pole* of the needle is attracted *downwards*, as well as to the north, and assumes a position almost vertical, that is, making an angle with the plumb line of about 20° : this inclination to the horizontal plane is called the *dip of the magnetic needle*.

These, and other phenomena, have been ascribed to the influence of a magnetic power in the earth: Dr. Halley regarded the globe as constituting a great magnet having four poles, two to the north and two to the south, at considerable and unequal distances from the poles of the earth. (*Miscellanea Curiosa*: as quoted by Dr. THOMSON on *Heat and Electricity*, p. 546.) Two of these poles, one to the north and one to the south, are supposed to be *fixed*, the other two *moveable*. Mr. Hansteen has adopted a similar hypothesis, and the changes in the direction and dip of the needle, or the *variation of the compass*, have been referred to such causes*: these, however, are subjects which it is unnecessary to pursue here, and I have only thus far adverted to them to remind the student of the necessity of taking the influence of the earth's magnetism into the account, in all cases where we speak of this power, and to explain another cause of the temporary and permanent production of magnetism in iron and steel, resulting exclusively from the earth's influence.

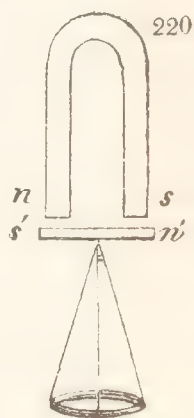
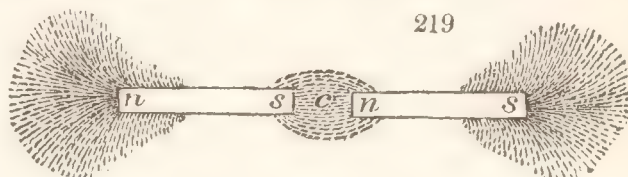
When a bar of soft iron is held nearly *vertical*, or in the *direction of the dipping needle*, its ends are no longer *indifferently* attractive of a poised magnet; but (so long only as it continues in or near that position) it is *polar*, the *lower end* of the bar being a *north pole*, and the *upper end* a *south pole*, and it affects the magnetic needle accordingly. We now need only place the bar in a *horizontal* position, and both ends then *indifferently* attract the poles of the needle; or in other words, the

* In the year 1660, the magnetic needle in London pointed exactly north and south, London being at that time in the *line of no variation*. Before that period, the variation was to the east, but after the year 1660, the variation became westerly, the line of no variation therefore has been progressively but slowly moving in a west-

erly direction, and has now passed to North America. At London, the westerly variation continued to increase till 1818, when it amounted to $24^{\circ} 30'$; this appears to have been its maximum, and since that time it has somewhat diminished. The *dip* has undergone corresponding changes; in 1773 the dip was $72^{\circ} 19'$; in 1830, $69^{\circ} 38'$.

induction of the earth is *neutralized* and vanishes. It is not uncommon to find bars of steel, which have long remained in a nearly vertical position, permanently magnetic; that is, *polar*; this is often the case with the poker and tongs; and there is a curious mode of making a magnet, dependent upon the same cause, which consists in holding a bar of steel in the direction of the magnetic dip, and, striking it whilst in that position, a few smart blows with a hammer; the upper and lower ends then become south and north poles. If a bar of steel already magnetized, and not in this position, be similarly treated, it loses its magnetism: and hence the necessity of caution in using good magnets, to avoid striking them or letting them fall, by which their magnetism is more or less weakened.

The manner in which the magnetic force emanates from the poles of a magnet is well illustrated, by placing two magnetized bars with their opposite poles about an inch asunder, under a sheet of writing-paper, and then sifting iron filings upon the paper; they will assume a peculiar and beautiful arrangement, showing the direction of the *magnetic curves*, (somewhat as in the annexed figure 219,) which is perfected by gently shaking or tapping the paper to assist their polar adhesions. If we place a piece of soft iron between the poles, and within the curves at *c*, it becomes, as already explained, magnetic, by induction. These curves or currents are well shown between the poles of what is commonly called a *horse-shoe magnet*, in which the magnetized bar is bent into that form. (fig. 220.) *n s* are its north and south poles; *s' n'* are the *induced* north and south poles of a bar of soft iron, commonly called the *holder*, and which, when applied to the magnet, is powerfully attracted. A scale-pan may be conveniently attached to the holder for determining the power of the magnet by the weight which it will sustain.



As iron and steel, when free from magnetism, are attracted only in consequence of induction, it follows that the degree of susceptibility to induction may be measured by the attraction which results from this property. With this view, Mr. Barlow (*Phil. Trans.*, 1822, p. 117) made a series of experiments to ascertain the relative attraction which different species of iron and steel had for the magnet, and obtained the following results, the relative magnetic power of each substance being expressed by numbers.

Malleable-iron	100	Hard blistered-steel.....	53
Soft cast-steel	74	Hard shear-steel	53
Soft blistered-steel	67	Hard cast-steel	49
Soft shear-steel	66	Cast-iron	48

Mr. Hatchett found that the *protosulphuret* and *phosphuret* of iron were susceptible of receiving and retaining magnetism; in this respect, therefore, they resemble the magnetic oxide of that metal, and steel: the peroxides, the persulphurets, and plumbago, natural and artificial, are not magnetic: his suggestions, in reference to the magnetic properties of the above compounds, and of the circumstances which interfere with those of the varieties of cast-iron, deserve further consideration. (*Phil. Trans.*, 1804.)

§ 18. ELECTRO-MAGNETISM*.

HAVING, in the preceding section, defined the meaning of the term *magnetism*, we now proceed to examine the *evolution of magnetism by electricity*; this important discovery was made in 1819, by Professor Ørsted, of Copenhagen.

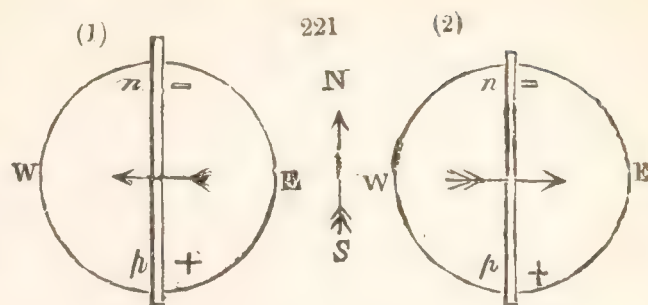
All the effects we are about to describe depend entirely upon *electricity in motion*, or upon *electric currents*, and are directly proportionate to the *quantity* of electricity: nothing of the kind is produced by electricity of *tension*, nor are they apparently increased by increasing the *intensity* of the current. Hence, for their development, voltaic electricity is infinitely more effective than common electricity; and those forms and conditions of the voltaic arrangements which are calculated to produce *quantity* rather than *intensity*, are required; hence also *perfect metallic contact* of the conductors employed must be observed.

When a wire transmitting the volta-electric current (and which may be called the *connecting wire*,) is brought near a common magnetic needle, it has the power of attracting and repelling it, in obedience to very peculiar laws. If a magnetic needle be left to take its natural direction, and then a straight portion of the connecting wire be brought *above and parallel to it*, the end of the needle which is next the negative pole of the battery moves towards the *west*, and that, whether the wire be on the one or other side of the needle, so that it be above and parallel to it. If the connecting wire be sunk on either side of the needle, so as to come into the *horizontal plane* in which the needle is allowed to move, there is no motion of the needle in that plane, but the pole of the needle attempts to move in a *vertical circle*, and but for the imperfect suspension, and the earth's magnetism, would do so. When this wire is on the *east* of the needle, the pole next the negative end of the battery is *elevated*, and when on the *west* of the needle it is *depressed*. If the connecting wire be now sunk *below the level of the needle*, similar attractions and repulsions take place, but in opposite directions to those followed when it is above. The pole of the needle opposite the negative end of the battery now moves *eastward*, whatever the position of the wire, so that it be restricted as above.

In discussing the relations of the electric and magnetic currents indicated by this experiment, it may be useful, instead of indiscriminately using the terms north and south, east and west, and negative and positive, to employ them in reference to the following position. If we stand with the face towards the north, and the current of electricity pass in the same direction, that is, from the south to the north (parallel with the magnetic meridian,) then the magnetic needle, when *above* the electric current, will turn to the *left*, or to the *west*; and *below* the current, to the *right* or to the *east*; its *north* pole will be *elevated* when on the *east* side of the current, and *depressed* when upon the *west*, and will have a tendency, therefore, to *revolve* round the electric current in a direction from *east to west*, or from *right to left*.

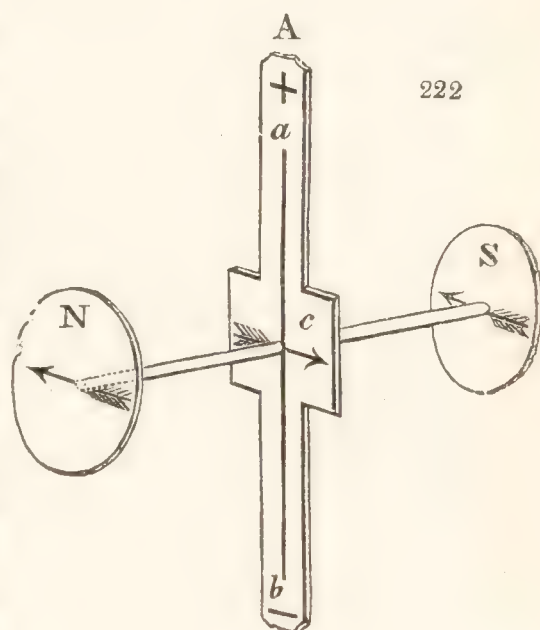
* The reader who may be desirous of historical details and references to authors, upon this subject, may advantageously consult Mr. Faraday's "Historical Sketch of Electro-magnetism," in the *Annals of Philosophy*. (New Series, ii.)

In the diagram (fig. 221) the electric current is supposed passing through the conducting-wire $pn(1)$, in the direction $s\ N$, in which case the magnetic needle, placed above it, has its marked or north pole deflected towards the *west*, and (as in 2), placed below it, towards the *east*.



The following contrivance of Dr. Roget is useful in assisting the memory respecting the details of these affections. AB (fig. 222) is a slip of card, on each side of which a line ab is drawn along the middle of its length, the end a being marked $+$, the end b $-$, and the centre c , being crossed by an arrow at right angles to it, directed as in the figure. Through the centre and at right angles to the plane of the slip of card, there is made to pass a slender stem of wood, at the two ends of which are fixed in planes parallel to the slip of card AB , the circular discs of card, marked respectively with the letters N and s , and with arrows parallel to, but pointing in a contrary direction to the one at c . The same marks must be put on the reverse of each of the three pieces of card, so that when held in different situations they may be seen without turning the instrument.

If the line ab be supposed to represent the galvanic wire (the direction of the current of electricity being denoted by the signs $+$ and $-$, at the ends of the line), the arrow at the centre will point out the direction in which that wire tends to move, when under the influence of the north pole of a magnet, situated at N ; or of a south pole situated on the other side at s : and *vice versâ*, the arrows at N and s will indicate the directions in which the north and south pole, respectively, tends to revolve round the galvanized wire in its vicinity, with relation to the direction of the current of electricity that is passing through it.

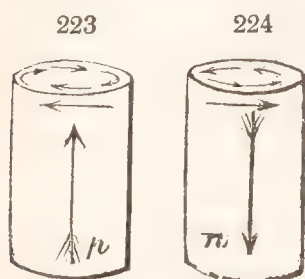


It must be observed that the poles N and s are here not considered as in connexion with each other, or as forming parts of one magnet; their operations are exhibited singly, and quite independently of each other. The advantage of this little instrument consists in its being capable of being held in any situation, and thus easily adapted to the circumstances of any fact or experiment of which we may wish to examine the theory.

All substances, which admit of the transfer of the electric current, exhibit similar phenomena; but the best conductors, or those which appear to afford the least resistance to the current, are those which become most powerfully magnetic: the metals, therefore, stand in the order of their electro-conductive powers; and when liquids are used, the best conductors among them are those by which the magnetic needle is most powerfully affected. The electric current itself, when passing through rare air, exhibits the same phenomena. Every part of the conductor, of course, exhibits similar phenomena, and everything through which the current is

passing; the connecting wire, therefore, so long as the current is passing through it, is everywhere attractive of iron-filings; and the voltaic pile itself acts upon the needle, precisely as the connecting-wire.

From the manner in which the needle is affected when placed parallel to either side of the electric current, it was inferred that a current of magnetism (as it may be termed) is put into motion by the electric current, so as to circulate, as it were, at right angles to the latter: hence Dr. Wollaston termed it *vertiginous magnetism*; or, as Mr. Barlow expressed it, the magnetic force exerts a *tangential* action. Let us, therefore,

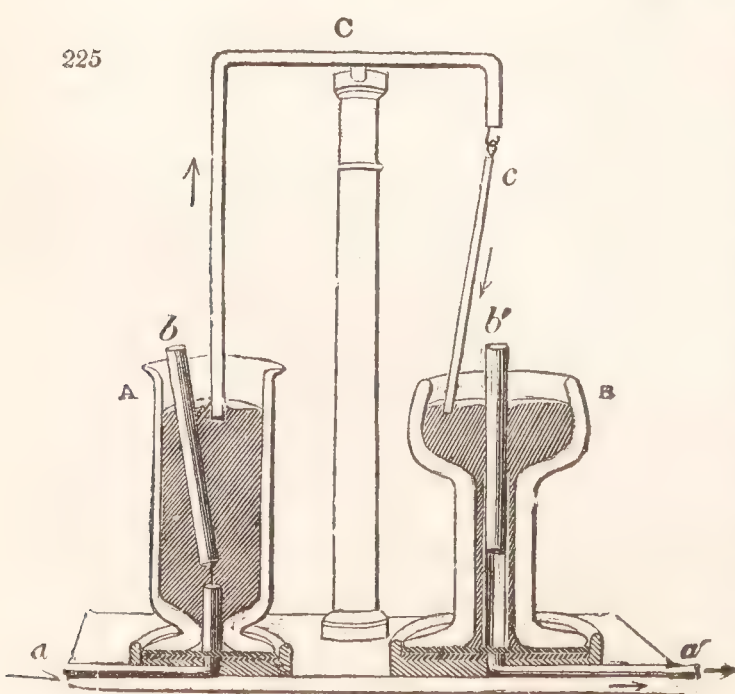


suppose fig. 223 to represent the conductor through which the electric current is passing from end to end in the direction of the dart *p*, then the small arrows will represent the direction of the circulating current of magnetism. In fig. 224 both currents are moving in the opposite direction. Supposing the wires or conductors above represented

placed side by side and parallel to each other, they will obviously be *magnetically repulsive*, because similar magnetic polarities (as shown by the horizontal darts) are opposed to each other; but if we invert either conductor, or, what amounts to the same thing, change the direction of the electric current in it, they will then become *magnetically attractive*, because the dissimilar magnetic polarities are then opposed to each other. So that two wires in which the electric current is passing in the same direction are magnetically attractive; and two wires, in which the electric current is passing in opposite directions, are magnetically repulsive.

Impressed with this view of the relative motions of the electric and magnetic currents, Mr. Faraday conceived that the pole of the magnet ought to revolve about the electric conductor, and the electric conductor about the pole of the magnet, and by the following ingenious apparatus he succeeded in the experimental verification of the theory*.

Fig. 225 represents two glass vessels, A and B, placed side by side, with their appendages. In A the motion of a magnetic pole round the



connecting-wire (or electric current) is produced, and in B the connecting-wire moves round the pole of the magnet. That a current of electricity may be established through the cup A, a hole is drilled at the bottom, and into this a copper pin is ground tight, which projects into the cup, and is rivetted below to a small round plate of copper, which forms part of the foot of the vessel, and communicates with the connecting-wire *a*. A small cylindrical and powerful magnet *b* has a piece of thread

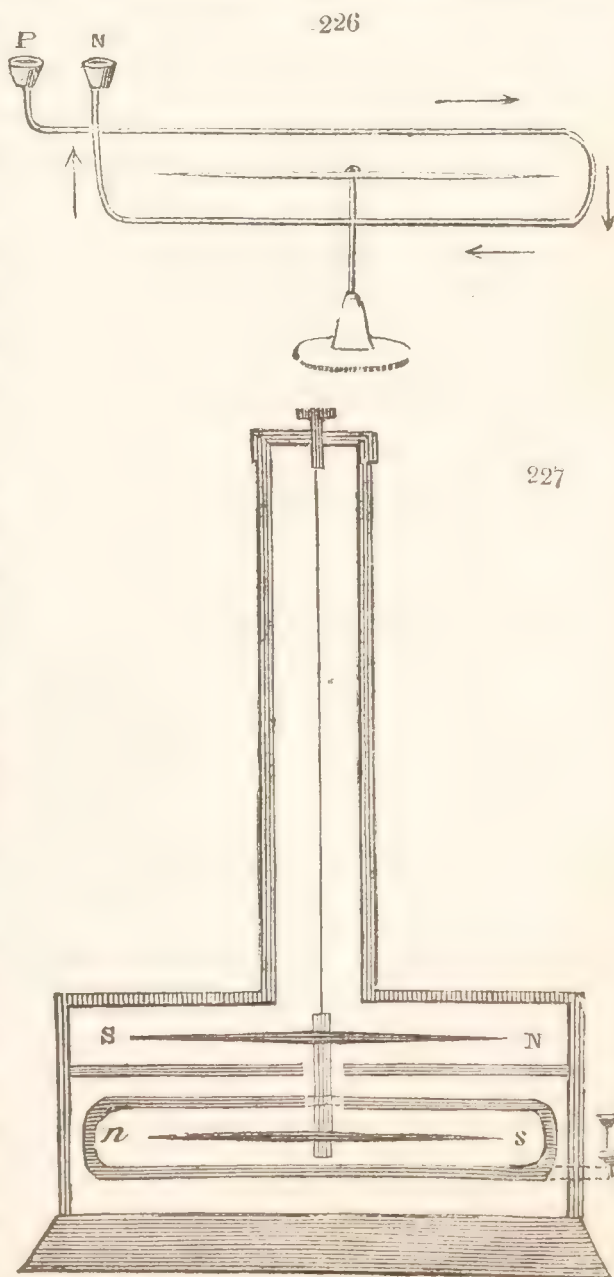
* Mr. Faraday's original papers on this subject will be found in the *Quarterly Journal of Science and the Arts*, vol. xii.,

pp. 75, 186, 283, and 416. The date of the first is September 11, 1821.

fastened to one of its poles, by which it is attached to the copper pin at the bottom of the cup, and so adjusted, that when the cup is full of clean mercury, the free pole b floats almost upright at the surface. The stem of the vessel B is tubular, and a copper socket is attached to its copper foot, in connexion with the conductor a' , which holds the magnet, b' , projecting above the centre of the mercury. In these cups of mercury, therefore, the two magnets are similarly arranged, except that in A the pole is moveable, and in B , fixed. c is a brass stem and cross-wire prolonged by a smaller wire into the cup of mercury A , on one side, and on the other into B , but on this side the conducting-wire c is suspended by a loop, so as freely to move round the end of the magnet b' . If a be now connected with the positive, and a' with the negative voltaic wire, so that the electric current may traverse the apparatus in the direction of the darts, the moveable magnetic pole b will revolve about the fixed conductor; and the moveable conductor c will revolve about the fixed magnetic pole b' . On changing the direction of the electric current, that of the respective rotatory motions will also be changed.

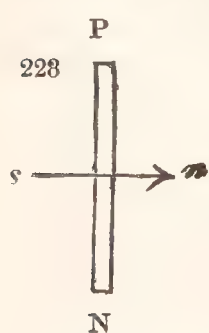
Since this discovery, a great variety of rotatory electro-magnetic apparatus has been suggested and contrived, in which the electric and magnetic currents are mutually made to produce the revolutions of conductors about each other, and about their own axes, in most of which volta-electricity, and in some, thermo-electricity is used: of these, a good account will be found in the *Library of Useful Knowledge* already quoted, and in Mr. F. Watkins' popular sketch of electro-magnetism and electro-dynamics.

Referring to the statement just given of the manner in which the magnetic needle is affected by the electric current, the construction and use of that valuable instrument the *galvanometer*, which has been so often referred to, and which was originally suggested by Schweigger, will easily be understood. In its simplest form it consists of a magnetic needle, so poised as to be affected by an electric current passing above and below it, as in fig. 226, where P and N are two small copper cups, each containing a little mercury, for the purpose of connexion with the voltaic or other source of the electric current, which moving in opposite directions in the upper and lower portions of the wire, as shown by the darts, will conspire in both cases to deflect the needle from its natural position, in the same direction, and to bring it into a position nearer to a right angle to the plane of the wires.



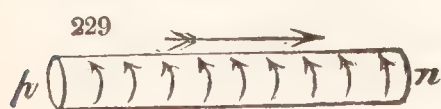
To *multiply* this effect, and to render the instrument a more susceptible indicator of feeble electric currents, the convolutions of the wire are multiplied, and the lateral transfer of electricity prevented, by coating it with silk, or sealing-wax; and instead of supporting the needle upon a pivot, it is suspended by a fine thread of silk, or, as suggested by Professor Ritchie, (*Phil. Trans.*, 1830, p. 218,) by a filament of spun-glass; the sensibility of the instrument is further increased by employing two needles, one above and the other within the coil, and placed parallel, but with their poles opposed, so as to neutralize the magnetic influence of the earth: to this instrument a divided circle is so attached as to enable the observer readily to read off the deviation. This form of galvanometer, or *electro-magnetic multiplier*, is shown in fig. 227 (in section), *n s* is the lower needle, surrounded by the coil of wire, and connected with the upper needle, *s n*, by an intermediate piece of straw, which passes through the upper part of the horizontal coil, and through the circular card above it, on which the graduated circle is drawn, and is attached to the torsion filament suspended from a screw, supported by the frame of the instrument.

From the direction of the *magnetic* as opposed to the *electric* current, it is obvious that an iron or steel needle placed *transversely* to the connecting-wire, as in fig. 228, will acquire magnetic *polarity*, and that if



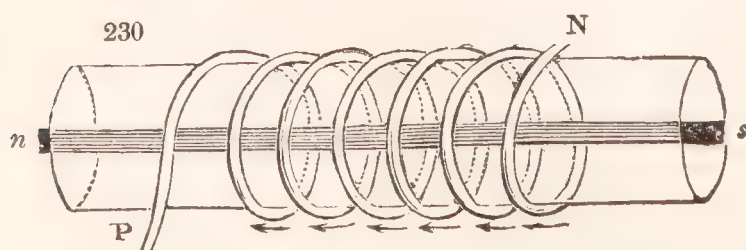
P N represent the conducting-wire, and *s n* the needle, the nature of its polarity will depend upon its being *above* or *below* the electric current. But in thus making a magnet, either temporarily of iron, or permanently of steel, a great increase of power is obtained by winding the connecting-wire (which in this case must be covered with silk to prevent contact of the metallic surfaces) round the iron bar, in the form of a close spiral, the effect of which will be,

in the first place, a close assimilation in the coil itself to a magnetic needle, and in the next a great increase in the general magnetic effect, as will be apparent from the following considerations. Let *p n*, fig. 229,



represent a straight conducting-wire, through which an electric current is passing in the direction of the large dart; the small darts will then show the direction of the magnetic

influence or vortex: if we now coil this wire into a spiral the magnetism will tend the same way in each convolution, as in fig. 230, where the conducting-wire, (in which the direction of the *magnetic* current is indicated by the darts,) is supposed to be wound spirally round a glass tube,



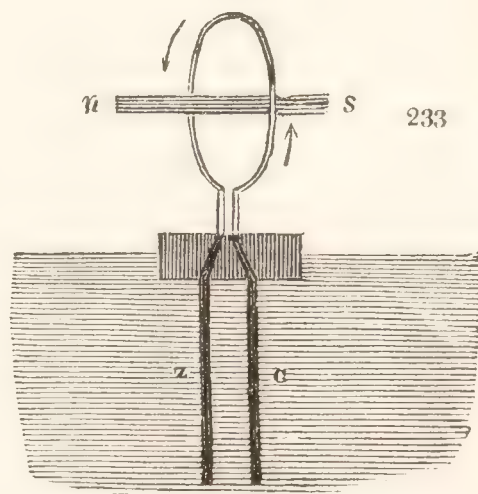
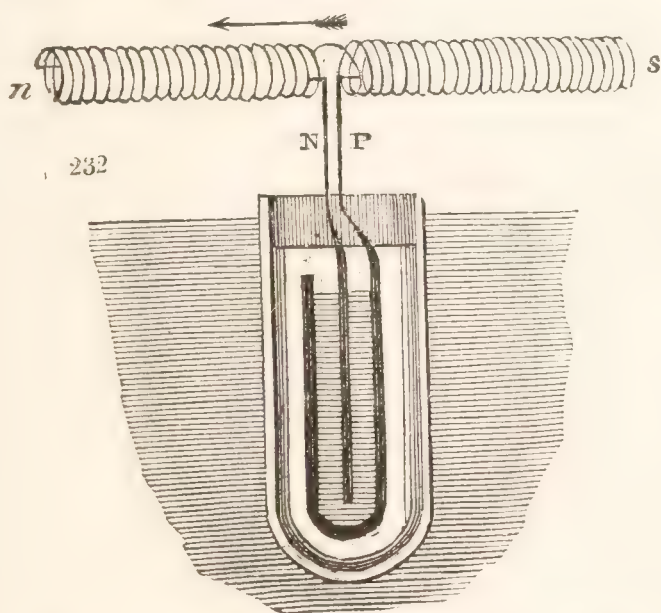
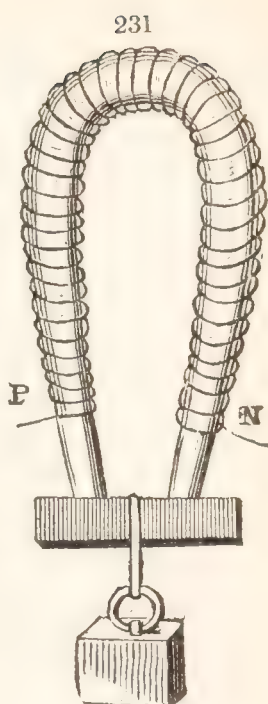
and where *n s* represents a steel bar in the axis of the tube and spiral, in which case it becomes a powerful magnet. If a glass tube thus surrounded by a coil of wire traversed by an ade-

quate electric current be held *vertically*, it will actually draw up an iron needle and retain it in its axis, against the force of gravity.

If such a wire be wound round a bar of soft iron, it is rendered a very powerful magnet during the passage of the electric current; and by

employing a bent bar of iron, (fig. 231,) and connecting the extremes of the wire P and N with the positive and negative mercurial cups of the single voltaic plates shown in fig. 169, a most powerful form of the horse-shoe magnet is obtained.

From the description of the heliacal or spiral arrangement just given, we can understand how a voltaic magnet may exactly resemble a common magnet, in its obedience to other magnets and to the earth's polarity. This is well shown in De la Rive's *floating electro-magnet* (fig. 232), in which the copper cup and zinc plate forming the simple voltaic circle, is inserted into a glass cylinder adapted for floating in water: the ends of the spiral being soldered to the wires N P. Here the spiral represents the magnetic needle placing itself in the magnetic meridian, and being obedient to another magnet brought to either of its poles.

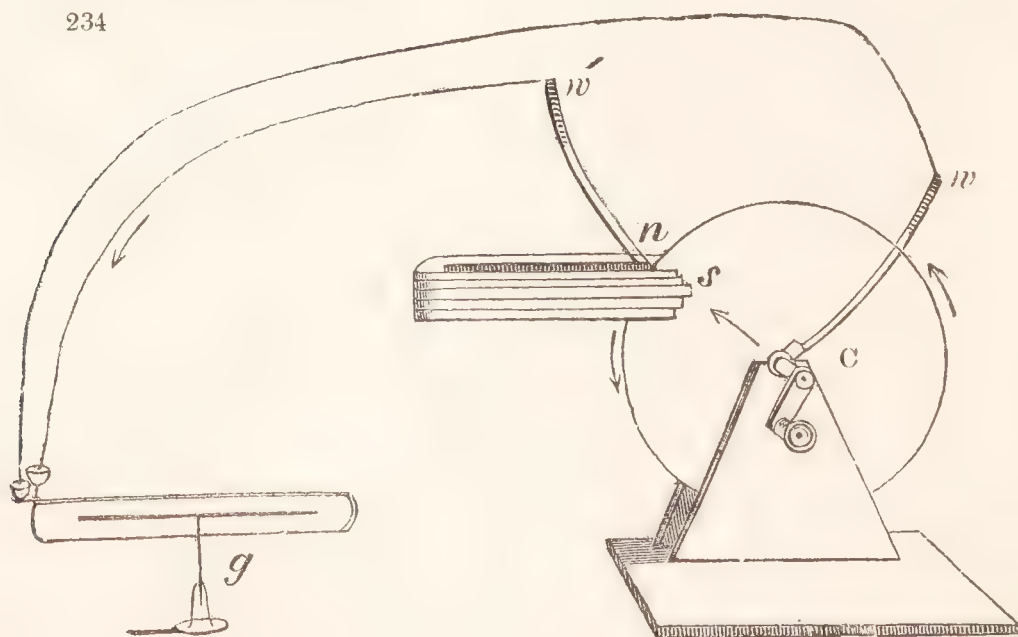


We have an interesting modification of this apparatus in De la Rive's single or *circular magnetic coil*, which may be constructed as follows. *z c* (fig. 233) are a zinc and copper plate attached to a piece of cork sufficient to float the whole apparatus, with the plates immersed in a basin of dilute sulphuric acid. A copper wire is soldered to the copper plate, and being covered with silk thread is formed into six or eight circular convolutions, its other end being soldered to the zinc plate. When this arrangement is floating in dilute acid, a current of electricity traverses the circles of wire in the direction of the darts, and a magnet *n s* presented horizontally to its axis causes the ring to move towards it, till it reaches its centre, where it pauses in a state of equilibrium. If we now withdraw the magnet, and reversing its poles, (whilst the ring is held in its first position,) pass it half way through the ring, it may possibly again remain in equilibrium, but the slightest change of position causes it to move with an accelerated velocity towards the pole nearest to it, and getting clear of the magnet, is first repelled, then turning round so as to present its opposite face to the magnet, it is attracted, and passing again over the pole of the magnet, rests in equilibrium at its centre, or at what may be called the magnetic equator. In the first position it was equally attracted by the two poles, and in the second equally repelled.

§ 19. MAGNETO-ELECTRICITY*.

UNDER this term, I shall describe another branch of electrical science, vying in interest and importance with the discovery of Ørsted detailed in the last section, and being in fact the converse of it, namely, *the production of electricity by magnetism*, for which we are exclusively indebted to Faraday. (*Phil. Trans.*, 1832.)

From the statements in the last section, it is evident that magnetism is in some way produced by electricity in motion; now it occurred to Mr. Faraday, in consequence of certain phenomena which he observed, and which he has described under the terms *volta-electric*, and *magneto-electric induction*, that magnetism in motion ought to produce an electric current, and he succeeded in verifying this important conclusion as follows: a long spiral coil of copper-wire, covered as in the former experiments with silk, was connected by its extremities with the galvanometer, the deflection of which would of course announce a current of electricity in the spiral and wires connected with it: he now found, that in the act of introducing the pole of a powerful bar-magnet within the coils of the spiral, a deflection of the galvanometer took place in one direction, and in the act of withdrawing it took place in the opposite direction; so that each time the conducting-wire cut the magnetic curves, a current of electricity was, for the moment, produced in it. He afterwards devised the following curious modification of this experiment: *c* (fig. 234) is a copper plate so mounted as to admit of revolving upon



its axis; *n s* are the poles of a powerful horse-shoe magnet, so placed as to admit of the revolution of the circumference of the plate between them; *w w'* are conducting wires, one of which is retained in perfect metallic contact with the axis, and the other with the circumference of the plate at the point between the poles *n s*. These wires terminate in

* Any extended details upon this extremely curious subject would be misplaced in a *Manual of Chemistry*: I must, therefore, refer for them to Faraday's first

series of experimental researches in electricity, read before the Royal Society, on the 24th of November, 1831, and published in the *Phil. Trans.* for 1832, p. 125.

the galvanometer *g*. When the copper plate is made to revolve from right to left, a current of electricity is produced, in the direction of the arrows, and deflects the galvanometer accordingly. If either the revolutions of the plate, or the poles of the magnet be reversed, the electric current moves in the opposite direction*.

Faraday not only succeeded in obtaining galvanometrical indications of an electric current, but, by another modification of the arrangement in which the electric current was induced by an electro-magnet, he actually succeeded in obtaining the electric spark. (*Phil. Trans.*, 1832, p. 132.) The electric spark was afterwards obtained from a common magnet, by Nobili and Antinori, and in this country by Professor Forbes. (*Phil. Trans. Edinb.*, 1832.) For this purpose, a helix of copper wire was formed round the middle of the soft iron holder of a powerful horse-shoe magnet; on making and breaking the contact between the holder and the magnet, magnetism was alternately created and destroyed within it; at these periods of transition, electric currents were induced in the helix, and on so arranging the conducting-wires as at these moments to make and break contact with mercury, a brilliant spark was observed at each motion of the holder. By making the poles of a powerful horse-shoe magnet revolve rapidly before a soft iron armature supplied as in the former case with a helix, or what is still better, causing the armature and helix to revolve before the poles, an electric current is obtained, which not only gives continuous sparks, but ignites wire, decomposes water, and produces powerful shocks. These *magneto-electric machines*, whilst they furnish a beautiful illustration of the production of electricity by moving magnetism, seem also to promise some advantage in the medical applications of electricity. They have also been applied to the purpose of obtaining instantaneous light, by causing the spark to inflame the wick of a small spirit-lamp, and it appears probable that they may be used as sources of electricity for telegraphic and chemical purposes.

One of the best forms of the magneto-electric machine is that contrived by Saxton, which has been figured and described by Daniell, (*Introduction*, § 834,) as follows:—

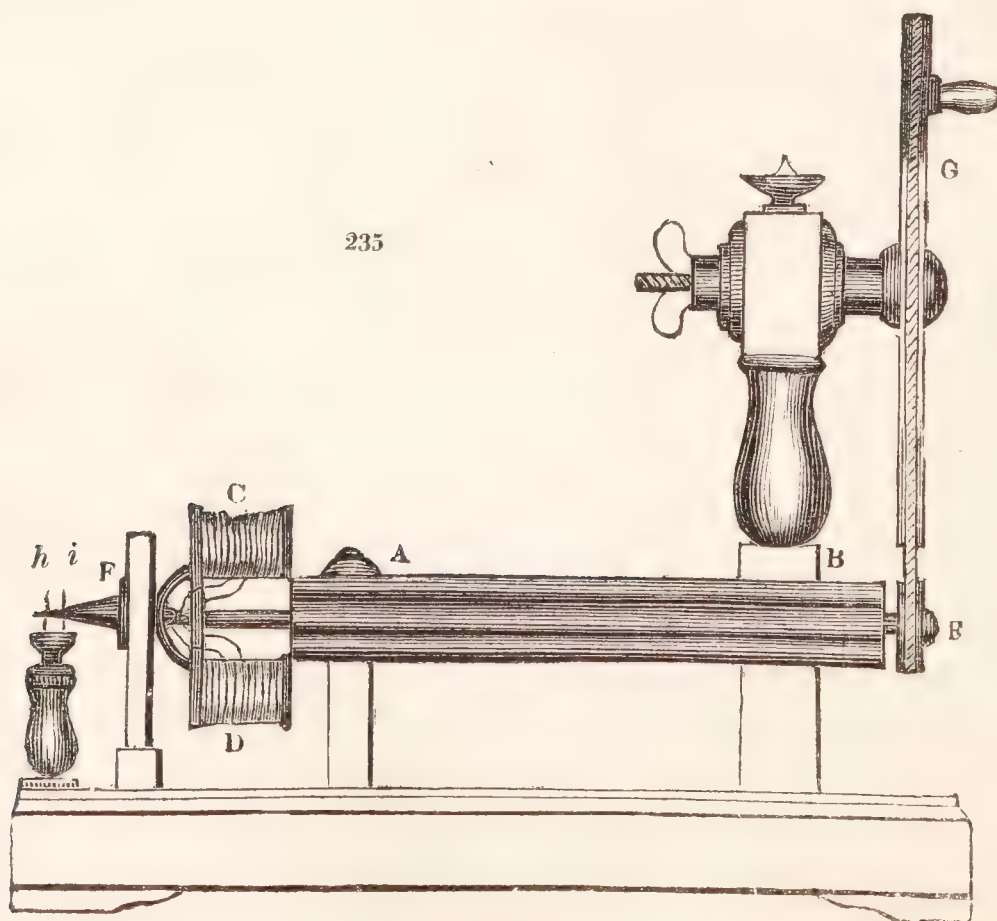
“A very powerful horse-shoe magnet, formed of numerous steel plates closely applied together, or an electro-magnet of soft iron of the same form, is placed in a horizontal position. An armature or bar of the purest soft iron has each of its ends bent at a right angle, and is mounted in such a way that the surfaces of those ends are directly opposed, and close to the poles of the magnet; in this position it may be made to rotate rapidly in a vertical direction, by means of multiplying wheels and an endless band. Two series of copper-wires, covered with silk, are wound round either end of this bar, as compound helices. The extremities of these wires having the same direction, are connected together, and with a small circular disc rotating with the armature in a cup of mercury, with which it is therefore

* In the year 1824, M. Arago discovered that a magnet suspended over, and parallel to the surfaces of a horizontal rotating copper plate, acquired a tendency to revolve in the same direction with the plate; and also that a rotatory magnet tended to give a similar rotatory motion to a contiguous

disc of copper. (*Phil. Trans.*, 1825, p. 467.) These phenomena are explained by the electric currents induced in the copper plate by its rotation within the magnetic curves, which currents flow at right angles to the direction of the motion. (FARADAY, *Phil. Trans.*, 1832, p. 146.)

in metallic communication in every position of the disc. The other extremities of the wires are united together, and passing without metallic contact through the spindle upon which the apparatus turns, terminate in a small slip of copper with two opposite points placed at right angles to the axis. These, in the act of rotation, alternately dip into, and rise above, the mercury in another cup, which may be connected with the first at pleasure by means of a copper wire. By the laws of magnetic induction, the armature becomes a temporary magnet whenever its bent ends are opposite the poles of the magnet, and ceases to be magnetic when they are at right angles to them. The momentary generation and destruction of the magnetic force, which will be oppositely directed in the bar as its opposite ends become opposed to the same poles in the act of rotation, must, by the laws of magneto-electric induction, induce corresponding opposite electric currents in the copper wire if the circuit be complete, by the immersion of the points at the moment of their passage. The points are so arranged that, standing nearly at right angles to the revolving bar, they just rise from the mercury as its ends become opposed to the poles of the magnet, and the circuit being thus suddenly broken at the moment of the electric wave, the current passes in the form of a brilliant spark."

The following figure represents a section of this magneto-electrical machine. *A B* is the horse-shoe magnet. *C D* the armature of soft iron, standing in a transverse direction to the poles of the magnet. *E F* is the spindle upon which it revolves by means of the multiplying wheels, *E G*. *h* and *i* are the metallic wheel and points by which connexion is made and broken between the mercury cup, *K*, and the ends of the coils of wire round the armature, *C D*.



By means of this magneto-electrical machine, all the well-known effects of voltaic currents may be very commodiously produced. When

the communication is made between the spindle and the revolving disc by means of a fine platinum wire instead of the dipping points, the wire may be maintained at a red-heat; although the effect being produced by alternating currents in opposite directions, a kind of pulsation, or intermission of the light, may be discerned. Upon making the communication between the two mercury cups by means of copper cylinders grasped in the hands, a continued painful contraction of the muscles of the arms takes place, which destroys voluntary motion, and, under certain circumstances, is perfectly intolerable. If the currents be transmitted into liquid electrolytes by means of platinum electrodes, they are readily decomposed; but in consequence of the alternate reversion of their direction, the *anions* and *cations* are mixed together. This, however, may be avoided, by turning up one of the points of the axis, when one of the currents will be cut off, and half the power destroyed, but the usual results of polar decomposition will be obtained. The amount of decomposition in this, as in all other cases, is in proportion to the quantity of electricity which circulates. By means of an electro-magnet and a constant battery which was capable of decomposing water by the primary current at the rate of eleven cubic inches of the mixed gases per minute, four cubic inches have been obtained in the same time by this secondary force.

From the manner in which a magnet in motion induces an electric current, it was presumed that the earth's magnetism might be rendered subservient to the same purpose, and Mr. Faraday found that a soft iron cylinder, introduced into the helix, as above described, and placed in the direction of the dipping needle, occasioned a deviation in the galvanometer; he even found that in a wire, or helix, moved at right angles to the dipping needle, so as to cut the magnetic curves of the earth, an electric current, sensible to the galvanometer, was induced; and that the rotation of a copper globe, or of a plate placed at right angles to the dip, produced the same effect; hence he concludes that the conducting matters of the earth's crust may be similarly affected by its diurnal revolutions, so as to induce electric currents flowing towards the poles, and suggests the possibility of the production of the Aurora, by returning electric currents from the poles into the atmosphere.

I must here bring to a conclusion this brief outline of electricity, and of the extraordinary phenomena arising out of it, such as the attractions and repulsions of masses of matter, chemical affinity, heat, light, and magnetism: how these attributes of matter are connected, or what is the true nature of their mutual dependence, are questions for future decision, when probably the whole subject will be simplified by referring them to one ultimate cause, in which it is not improbable that even gravitation may itself be included. From what has already been attained in this branch of science, some anticipations may be fairly formed of its probable progress hereafter; and if, among these, we admit the possibility of a more unlimited command than we at present possess over the production or extrication of this extraordinary agent, our speculations would assume a very extensive and interesting aspect; its mechanical and chemical powers would be perpetually called into action; the former as a substitute for steam, wind, and water; and the latter for the more sluggish or circuitous and difficult methods of ordinary decomposition; its single application to the evolution of oxygen and hydrogen from water,

and of chlorine and sodium from salt, would alone work wonders; and even as a direct source of heat and light, its applications and uses would be gigantic and endless; whilst the facility of its conveyance and transmission, its ubiquity, and its varied attributes in those different states which we, for want of more explicit knowledge of their cause, have termed *quantity* and *tension*, seem to point it out as of unlimited application to human uses*.

* During the progress of this sheet through the press, the Nineteenth, Twentieth, and Twenty-first Series of FARADAY'S *Experimental Researches in Electricity* have been published in the *Philosophical Transactions* (Part I. 1846). They relate to *The magnetisation of light, and the illumination of magnetic lines of force; and to certain new magnetic actions, including the magnetic condition of all matter.*

The fundamental experiment, showing that a ray of light may be electrified and magnetised, and that lines of magnetic force may, in the language of the author, be rendered luminous, is as follows. A ray of light, from an argand lamp, is first polarised in the horizontal plane by reflexion from a glass mirror, and then made to pass through a piece of glass of great density, composed of silicated borate of lead, about two inches square and half an inch thick, having flat and polished edges; on emerging from this medium, it is viewed through a Nichol's eye-piece, capable of revolving on a horizontal axis, so as either to intercept or transmit the ray: this glass is so placed between the poles of a very powerful electro-magnet, that the lines of magnetic force resulting from their combined action shall nearly coincide with the course of the ray passing through it: when the eye-piece is so turned as to render the image of the flame invisible, it immediately becomes visible on developing the force of the magnet by sending a current of electricity through its coils, but on stopping the electric current it again instantly vanishes. The results of an elaborate series of investigations are detailed in this paper, establishing a direct relation between light and the magnetic and electric forces.

In the paper on "New Magnetic Actions," it is shown that every substance placed between the poles of a powerful magnet is influenced in one of two ways: it either takes a position coincident with the magnetic forces, as is the case with a bar of iron, and other bodies usually called magnetic; or it places itself at right angles to the line of forces, as is the case with a bar of glass, of bismuth, and apparently of every other body: the former of these bodies the author distinguishes as *magnetics*, the latter as *diamagnetics*, and their respective positions between the poles are termed *axial*

and *equatorial*: he examines a vast variety of simple and compound substances, of solids, liquids, and gases, with reference to this classification—the number of *simple magnetics* is very limited, consisting of iron, nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, and osmium: all other bodies are *diamagnetic*, corresponding to bismuth, but with varying intensities: the following exhibit it in increasing degrees according to the order of their enumeration: arsenic, ether, alcohol, gold, water, mercury, flint glass, tin, lead, zinc, antimony, phosphorus, bismuth.

As respects compound bodies, Faraday found that their magnetic properties depended upon those of their elements, and that they are either magnetic or diamagnetic according as one or other of those conditions prevail in their component parts. Thus iron retains its magnetic power when it enters into combination with other bodies of the diamagnetic class, the two forces opposing each other and the resulting effect being due to the difference in their power, so that the oxides and salts of iron are still more or less magnetic, and the latter even when in aqueous solution; but the water, which is a diamagnetic, may be present in such proportion as to neutralize the magnetic power of the iron, so that such solution will be indifferent as to its position in the magnetic curves, pointing neither axially nor equatorially.

In one respect the diamagnetic action presents a remarkable contrast to the magnetic, namely, in being devoid of any trace of polarity, for the particles of two diamagnetics when jointly under the influence of the magnetic forces manifest no signs of attraction or repulsion towards each other.

All the facts set forth in this paper are resolvable by induction into the general law, that while every particle of a *magnetic* body is *attracted*, every particle of a *diamagnetic* body is *repelled* by either pole of a magnet: these forces continue as long as the magnetic power is sustained, and cease on the cessation of that power, standing therefore in the same general antithetical relation to each other as the positive and negative conditions of electricity, the northern and southern polarities of ordinary magnetism, or the lines of electric and magnetic force in magneto-electricity.

CHAPTER V.

OF SIMPLE SUBSTANCES.

UNDER the term *simple* or *elementary* substances, we include all bodies which have hitherto resisted decomposition, or resolution into simpler forms of matter; and although it may be presumed that some, or perhaps many of them, are in reality compounds, and that they will be proved to be so, as science advances and our means of investigation are extended and improved, yet in the present state of our knowledge, in which experiment and not hypothesis is resorted to as the ultimate test, these substances, numerous and varied as they are, having afforded no satisfactory indications of a compound nature, must be considered (not as *undecomposable* but) as *undecomposed*. They amount to fifty-five in number, and are alphabetically arranged in column B of the following table, preceded by their symbols in column A, and followed in column C by the equivalents, or atomic weights, which I shall employ in the sequel; it will be seen that, with very few exceptions, they correspond with the numbers adopted by Gmelin, in the latest edition of his Handbook, (*Handbuch der Chemie*, Heidelberg, 1843-45,) and are but little at variance with those employed by Professor Graham, (*Elem. Ch.*, London, 1842,) and by most other elementary writers in this country, as shown in column E: these all have reference to hydrogen as = 1. The atomic weights of Berzelius, having reference to oxygen as = 100, are contained in column F. When any material change has been made in the equivalents formerly employed, the reason for such alteration will be found under the head of the substance concerned.

A	B	C	D	E	F
Al.	Aluminum	14	14	13·72	171·17
Sb.	Antimony (Stibium)	129	129	129·24	806·45
As.	Arsenic	75	75	75·34	470·04
Ba.	Barium	69	68·6	68·66	856·88
Bi.	Bismuth	213	213	71·07	886·92
B.	Boron	11	10·8	10·91	136·25
Br.	Bromine	78	78·4	78·39	978·30
Cd.	Cadmium	56	55·8	55·83	696·77
Ca.	Calcium	20	20	20·52	256·02
C.	Carbon	6	6	6·13	75·40
Ce.	Cerium	46	46	46·05	574·70
Cl.	Chlorine	36	35·4	35·47	442·65
Cr.	Chromium	28	28	28·19	351·82
Co.	Cobalt	30	29·5	29·57	368·99
Ta.	Columbium (Tantalum)	185	185	184·90	2307·44
Cu.	Copper (Cuprum)	32	32	31·71	395·70
F.	Fluorine	19	18·7	18·74	233·80
G.	Glucinum	5	4·7	26·54	331·26
Au.	Gold (Aurum)	200	199	199·21	2486·02
H.	Hydrogen	1	1	1	12·48

A	B	C	D	E	F
I.	Iodine	126	126	126·5	1579·50
Ir.	Iridium	99	99	98·8	1233·50
Fe.	Iron (Ferrum)	28	27	27·18	339·21
La.	Lanthanum	44			
Pb.	Lead (Plumbum)	104	104	103·73	1294·50
Li.	Lithium	7	6·4	6·44	80·33
Mg.	Magnesium	12	12	12·69	158·35
Mn.	Manganese	28	28	27·72	345·89
Hg.	Mercury (Hydrargyrum)	100	100	101·43	2531·65
Mo.	Molybdenum	48	48	47·96	598·52
Ni.	Nickel	28	29·5	29·62	369·68
N.	Nitrogen	14	14	14·19	177·04
Os.	Osmium	100	99	99·72	1244·49
O.	Oxygen'	8	8	8·01	100·00
Pd.	Palladium	54	53·3	53·36	665·90
P.	Phosphorus	32	32	31·44	196·14
Pt.	Platinum	99	99	98·84	1233·50
K.	Potassium (Kalium)	40	39·2	39·26	489·92
R.	Rhodium	52	52	52·20	651·39
Se.	Selenium	40	40	39·63	494·58
Si.	Silicium	15	15	22·22	277·31
Ag.	Silver (Argentum)	108	108	108·30	1351·61
Na.	Sodium (Natrium)	24	23·2	23·31	290·90
Sr.	Strontium	44	44	43·85	547·29
S.	Sulphur	16	16	16·12	201·17
Te.	Tellurium	64	64	64·25	801·76
Th.	Thorium	60	59·6	59·83	744·90
Sn.	Tin (Stannum)	59	59	58·92	735·29
Ti.	Titanium	24	24	24·33	303·66
W.	Tungsten (Wolfram)	100	96	94·80	1246·25
U.	Uranium	60	60	61·00	2711·36
V.	Vanadium	68	68·6	68·66	856·86
Y.	Yttrium	32	32	32·25	402·51
Zn.	Zinc	32	32·2	32·32	403·23
Zr.	Zirconium	23	22·4	33·67	420·20

The preceding list admits of an obvious and useful division into *substances which are and which are not metallic*, and there are general analogies among the *metals* which enable us to subdivide them into classes; but with respect to the *non-metallic* bodies, the subdivision is more difficult, and the principles of classification usually applied to them are, in many respects, objectionable. If their arrangement be founded either upon their general electrical or chemical relations, as, for instance, into *electro-negative* and *electro-positive* bodies (anions and cations), or into *supporters of combustion* and *combustibles*, or into *acidifying* and *acidifiable* substances, difficulties occur in the details, which are of much practical inconvenience; for the electrical arrangement brings together substances extremely dissimilar in their chemical characters, such, for instance, as oxygen and sulphur, both of which are electro-negative bodies,

or *anions*; and the chemical arrangement leads us at one time to class oxygen with sulphur, both being supporters of combustion; and at another to separate them, in consequence of oxygen being eminently a supporter of combustion, and sulphur as eminently a combustible. Again, in regard to the terms *acidifying* and *acidifiable*; oxygen and chlorine are included among the former, and hydrogen and sulphur among the latter; yet oxygen and chlorine combine with each other to form acids, and neither of them being, in any usual sense of the term, *combustible*, it is difficult to say which is the acidifying and which the acidifiable element: the compound of hydrogen and sulphur is also acid, yet both hydrogen and sulphur are *combustible*, and hydrogen is *acidifiable* in respect to chlorine, as sulphur is in respect to oxygen. In all these arrangements, too, nitrogen stands out (regarding it as elementary), as an obstinate exception; it is *acidifiable* by oxygen, but it is *alkalifiable* by hydrogen; it is neither *combustible*, nor is it a *supporter of combustion*; and its electro-chemical relations are doubtful: indeed the distinction between some of these bodies and the *metals* is not in all cases very definite: there are strong analogies, for instance, between arsenic, and selenium, and sulphur, so that Berzelius actually arranges selenium with the metals; and some forms of carbon approach so closely in their characters to those of a metal, that Döbereiner speaks of *carbonium* as a metal. Under these difficulties, the electrical and chemical analogies of the unmetallic elements have been rejected as the basis of classification, and they have been arranged in reference to their supposed importance as chemical agents, and to convenience of discussion: Berzelius divides them, generally, into *oxygen*, which he places by itself as a supporter of combustion, and into *inflammable substances*, in which he includes all the other elements; and then, adverting particularly to the *unmetallic* substances, he divides them into three classes, namely,—1. *Permanently elastic or gaseous bodies (Gazolyta)*: oxygen, hydrogen, nitrogen. 2ndly. *Metalloids*: sulphur, phosphorus, carbon, boron, and silicon. 3rdly. *Salifying substances, (Halogenia)*: chlorine, iodine, bromine, fluorine. Almost all agree in placing *oxygen* at the head of the list; but scarcely any systematic writers concur in the order in which they describe the remaining unmetallic elements; except, indeed, that they usually place *hydrogen* after oxygen. But the most important difference amongst them is, in what relates to the *compound substances*, some describing them along with, or immediately after, their respective elements: and others giving the abstract history of each element separately, and then referring to their mutual combinations. It would be useless to point out in detail the objections which may be made to each systematic arrangement, for, after all, that will be preferable which is best calculated to guide and assist the student in the acquisition of the leading facts and doctrines of the science, and which is, at the same time, most convenient for reference. Under these circumstances I have retained, with such modifications as the progress of chemistry has rendered necessary, the general plan adopted in the former editions of this work. Oxygen, and the bodies associated with it in many of their electrical and chemical habitudes, stand first on the list; and these are succeeded by the inflammable and acidifiable bases: they will be described in the following order:

1. OXYGEN.
2. CHLORINE, and its combinations with oxygen.
3. IODINE, and its combinations with oxygen and chlorine.
4. BROMINE, and its combinations with the three preceding substances.
5. FLUORINE, and its combinations with the four preceding substances.
6. HYDROGEN, and its combinations with the five preceding substances.
7. NITROGEN, and its combinations with the six preceding substances.
8. SULPHUR, and its combinations with the seven preceding substances.
9. SELENIUM, and its combinations with the eight preceding substances.
10. PHOSPHORUS, and its combinations with the nine preceding substances.
11. CARBON, and its combinations with the ten preceding substances.
12. BORON, and its combinations with the eleven preceding substances.

The origin of the *names* by which the simple substances are distinguished, will be found under their individual history, but it will be necessary here to advert to the general principles of *nomenclature* applied to their mutual combinations.

All the combinations of oxygen, chlorine, iodine, bromine, and fluorine, with the inflammables and metals, which are *not acid*, are called *oxides*, *chlorides*, *iodides*, *bromides*, and *fluorides*: the combinations of the inflammable substances with each other, and with the metals, are distinguished by the termination *uret*, as *sulphuret*, *phosphuret*, &c., and in some cases the combinations of certain metals with each other are similarly designated: thus we speak of *arseniurets*, *tellurets*, *antimoniurets*.

The different *proportions* of oxygen in the oxides are distinguished by a prefix derived from the Latin or Greek numerals; thus we have *protoxide*, *deutoxide* or *binoxide*, *tritoxide* or *teroxide*, for the first, second, and third stages of oxidizement; and the highest degree of oxidizement is termed *peroxide*; when the proportions of oxygen in an oxide are as 1 to $1\frac{1}{2}$, or 2 to 3, the compound is termed a *sesquioxide*. If the oxide is so constituted as to contain 2 atoms of base and 1 of oxygen, it is then termed a *suboxide*, or, more definitely, a *dioxide*; and if 3 atoms of base and 1 of oxygen, a *tritoxide*. The same distinctive nomenclature is applied to the chlorides, iodides, sulphurets, phosphurets, &c.

The names of the *acid* compounds of oxygen are derived from their bases, and where there is only *one*, it is usually designated by the termination *ic*; where there are *two* acids of the same base and oxygen, that containing the smallest proportion of oxygen is distinguished by the termination *ous*, and that containing the larger proportion by the termination *ic*; as *arsenious* and *arsenic acid*: where there are *more than two* acid compounds of the same base, more complicated terms are requisite, of which the nomenclature of the four principal acids of sulphur forms a good example; these are termed; 1. *hyposulphurous acid*; 2. *sulphurous acid*; 3. *hyposulphuric acid*; 4. *sulphuric acid*; and occasionally the acid containing the *maximum* of oxygen is further distinguished by the prefix *per* or *oxy*: thus we sometimes use the terms *oxychloric acid*, *permanganic acid*, &c.

The *saline* combinations of the acids ending in *ous* are distinguished by the termination *ite*, and those ending in *ic*, by the termination *ate*: thus we have a *hyposulphite*, a *sulphite*, a *hyposulphate*, and a *sulphate* of potassa, &c., and where the acid and base unite in more than one

proportion, a distinction similar to that applied to the oxides is resorted to; thus the compound of one atom of potassa and *two* of sulphuric acid is a *bisulphate* of potassa: that of *two* atoms of oxide of lead and one of nitric acid, a *dinitrate* of lead: these are also sometimes called *supersulphate* of potassa, and *subnitrate* of lead; but the preceding terms are more definite. Lastly, the same acid occasionally forms distinct compounds with the protoxide and peroxide of the same metal, forming *protosalts* and *persalts*. Thus we have a *proto-sulphate* and a *persulphate* of iron, &c. Other more complex cases of nomenclature occasionally arise out of the preceding, which, however, will be sufficiently intelligible when they occur, by reference to the context.

CHEMICAL SYMBOLS. In former editions of this work I have used a system of symbolic notation upon the principles suggested by Dr. Whewell (*Journ. Royal Inst.*, i. 437,) differing in some respects from that of Berzelius; but as the latter is now generally adopted, I shall for the future employ it. It will be seen by reference to the preceding table (p. 259,) that each elementary substance is represented by the initial letter of its Latin name; and that, where two or more elements have the same initial, a second smaller letter is used as a distinctive adjunct: thus C, Cl, Ca, Cd, Co, Cu, Ce, Cr, are the symbols of carbon, chlorine, calcium, cadmium, cobalt, copper (cuprum), cerium, and chromium; H and Hg, of hydrogen and mercury (hydrargyrum), &c.

These symbols are also used to indicate certain *definite quantities* of each of the elements: thus C and H indicate respectively one atom or equivalent of carbon and one of hydrogen, or 6 parts by weight of the former and 1 of the latter. O not only indicates oxygen, but 8 parts by weight, or one atom or equivalent of oxygen; and so on, as exhibited in the table already referred to.

Two or more equivalents of the same element are sometimes indicated by figures to the left of or preceding the symbol: thus 2O, 3H, 4C, imply 2 equivalents of oxygen, 3 of hydrogen, and 4 of carbon; but where symbols are placed together in the formulæ of compounds, the same end is commonly attained by placing small figures to the right of the elementary symbol: these figures are sometimes placed a little above and sometimes a little below the symbolic letter, but such distinction seems unnecessary: thus O₂, H₃, C₄, indicate 2 atoms of oxygen, 3 of hydrogen, and 4 of carbon.

By a proper collocation or combination of symbols, the formulæ of *compounds* are similarly expressed, aided by the introduction of a comma, or of this sign, +. Thus NO indicates a compound of 1 atom of nitrogen with 1 atom of oxygen, and NO₂, 1 of nitrogen and 2 of oxygen, and so on. CuO is the symbol of oxide of copper, (consisting of 1 atom of copper and 1 of oxygen,) and SO₃ is the symbol of sulphuric acid, (consisting of 1 atom of sulphur and 3 of oxygen,) and the compound of oxide of copper and sulphuric acid (or the sulphate of oxide of copper) may be written as follows, CuO SO₃; but in this case the elements of the salt are more distinctly announced by the interposition of a comma or + between the oxide and the acid, as CuO, SO₃, or CuO + SO₃. It is often convenient to use both the comma and the plus sign, as in the case,

for instance, of double salts; thus a double salt, consisting of 1 equivalent of sulphate of oxide of copper, combined with 1 of sulphate of oxide of iron, may be represented as follows: $\text{CuO}, \text{SO}_3 + \text{FeO}, \text{SO}_3$.

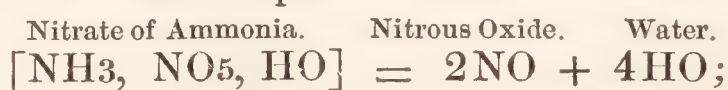
In the preceding formulæ the figures only affect the symbol to which they are immediately appended; where they are intended to apply to the entire compound, they are always placed before and in a line with the symbol of the compound; thus 3 atoms or equivalents of sulphuric acid would be written 3SO_3 ; and two atoms of oxide of copper 2CuO . The symbol $2 \text{CuO} + \text{SO}_3$ implies a salt containing 2 atoms of oxide of copper and 1 of sulphuric acid; the intervening + (or a comma) preventing the extension or influence of the figure 2 beyond the oxide of copper; and if our object were to imply 2 atoms of sulphate of oxide of copper, we should then use brackets; as $2 [\text{CuO}, \text{SO}_3]$.

In arranging the symbols, it is customary to let the basic or electro-positive constituent, or cation, precede the electro-negative constituent, or the anion of the compound: thus oxide of silver and chloride of potassium are written AgO , and KCl ; and sulphate of soda is written NaO, SO_3 , and not SO_3, NaO . The atoms of oxygen are sometimes indicated by dots placed over the symbol; thus, instead of writing NO_5 ,

for *nitric acid*, we use the abbreviation $\ddot{\text{N}}$. In like manner the compounds of *sulphur* have been denoted by, Berzelius, by commas; thus, sulphuretted hydrogen HS , he writes H ; and where he wishes to represent *two* equivalents of an element, they are sometimes denoted by a dash through or under its symbol; thus H or H , indicates 2 atoms of hydrogen. The *organic acids* he abbreviates by using the first letter of their name with a dash over it, thus $\bar{\text{T}}$ $\bar{\text{C}}$ $\bar{\text{F}}$ are the *tartaric*, *citric*, and *formic acids*.

Other symbolic abbreviations are occasionally used, especially in reference to certain compounds which act the part of simple supporters, or bases: thus Cy indicates *cyanogen*, instead of using its detailed symbol, C_2N ; and E , = *ethule*, in place of C_4H_5 , &c.: Aq . or simply q , is an abbreviation for water; and I have found it convenient to represent the acids in common use by associating an acute accent with their basic letter, as N' , S' , P' , C' , HCl' , for nitric, sulphuric, phosphoric, carbonic, hydrochloric acids, &c. The letters M and B are sometimes used generally for *metal* and *base*.

The great use of symbols is visibly as it were to present the elements of compounds, so that all their possible combinations may be traced with comparative facility, and their less obvious relations detected. They also facilitate the complex computations required in reference to the atomic constitution of various organic compounds, and often enable the teacher to present the student, at one view, with details which, in the ordinary mode of proceeding, would be verbose and complex. Thus the conversion by heat of 1 atom of nitrate of ammonia into 2 atoms of protoxide of nitrogen, and 4 of water is represented as follows:

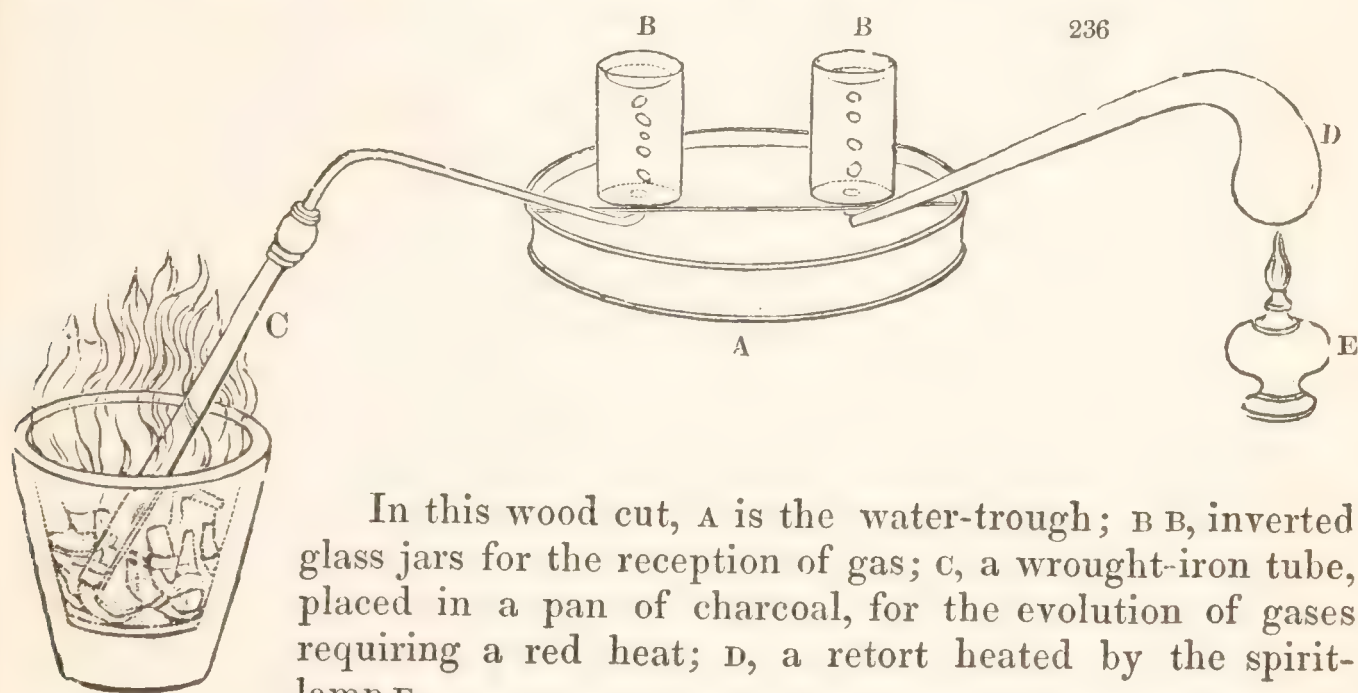


of such and similar applications of symbols, abundant instances will be found in the sequel.

PNEUMATIC APPARATUS. Of the simple substances which we are about to examine, four are known to us in the gaseous state, and amongst their combinations there are many which also assume that form; so that it will be necessary before we enter upon their history, to say a few words respecting the apparatus by which gaseous bodies are procured and examined.

The *hydro-pneumatic apparatus* consists of a japanned iron or copper vessel, of different shape and size according to the particular purposes for which it is intended, and containing a shelf perforated with holes, through which the gas may pass into inverted vessels properly placed for its reception.

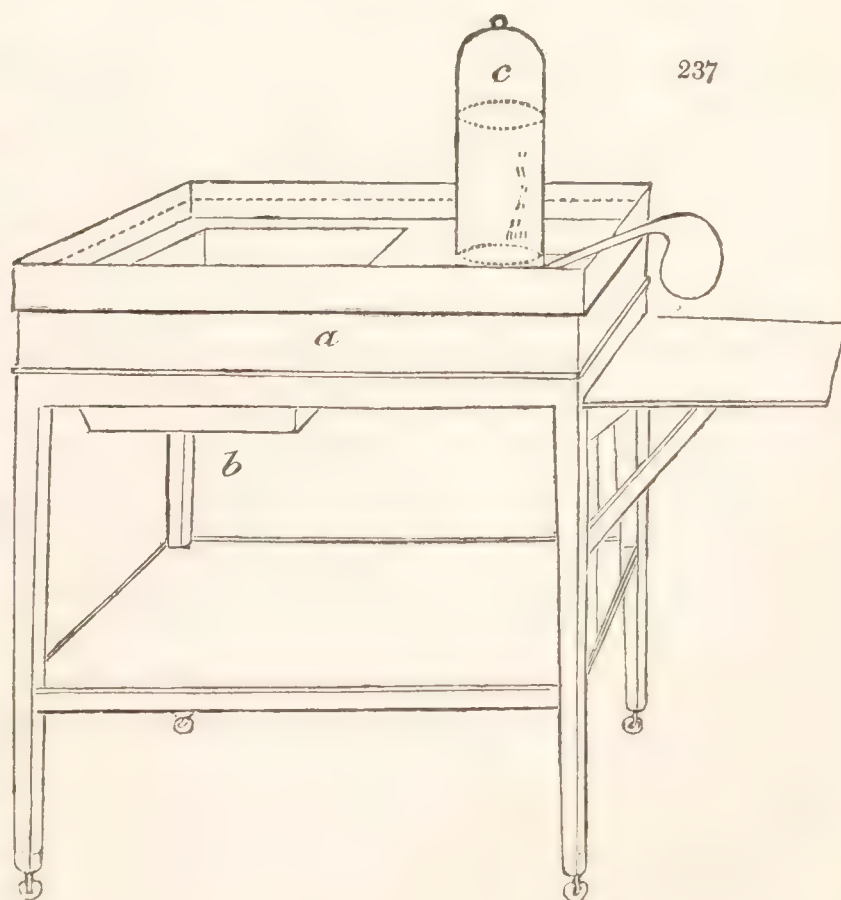
A shallow earthen-ware pan, or a wooden tub, or a vessel of what is termed enamelled iron, with one or more low cast-iron trivets to serve as a substitute for the perforated shelf to support the inverted air jars, are also very useful forms of the pneumatic trough.



In this wood cut, A is the water-trough; B B, inverted glass jars for the reception of gas; C, a wrought-iron tube, placed in a pan of charcoal, for the evolution of gases requiring a red heat; D, a retort heated by the spirit-lamp E.

For experiments, in which *large vessels* are employed for collecting or transferring gases, the annexed form of the apparatus (fig. 237) is most convenient: the trough is placed in a wooden frame or stand *a*; it has a deep part at *b*, and a shallow shelf, upon which the inverted jar may be placed over a groove, as at *c*.

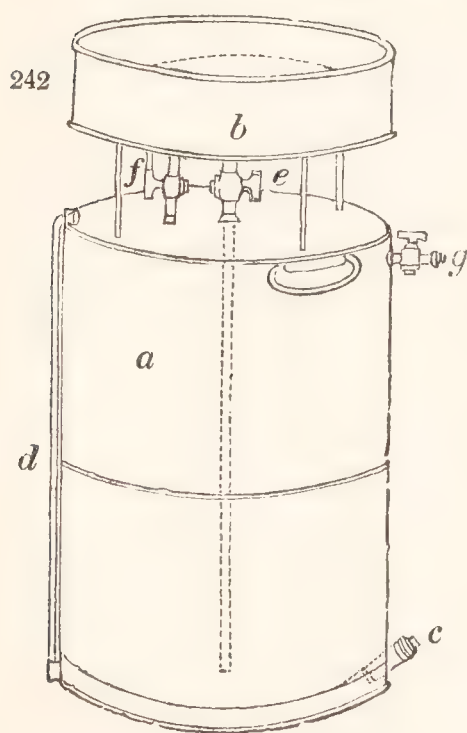
Vessels of various forms are employed for receiving, retaining, and measuring gases. Where it is intended to introduce different substances into the gas, they may be



of the form represented in figure 238, drawn into a neck with a glass-

stopper at top, and open at bottom. Some of these should be graduated into cubic inches, and supplied with a stop-cock, as in figure 239. For measuring small quantities of gases, tubes are employed, some of which should be divided into 100 equal parts, others into tenths and hundredths of a cubical inch, as in figs. 240 and 241.

Where large quantities of gases are required to be collected and preserved, we employ *gasholders* and *gasometers*. Fig. 242 represents Pepys's improved gasholder, made of japanned iron, or what is preferable, of zincd iron or of copper. It consists of a body or reservoir *a*, which

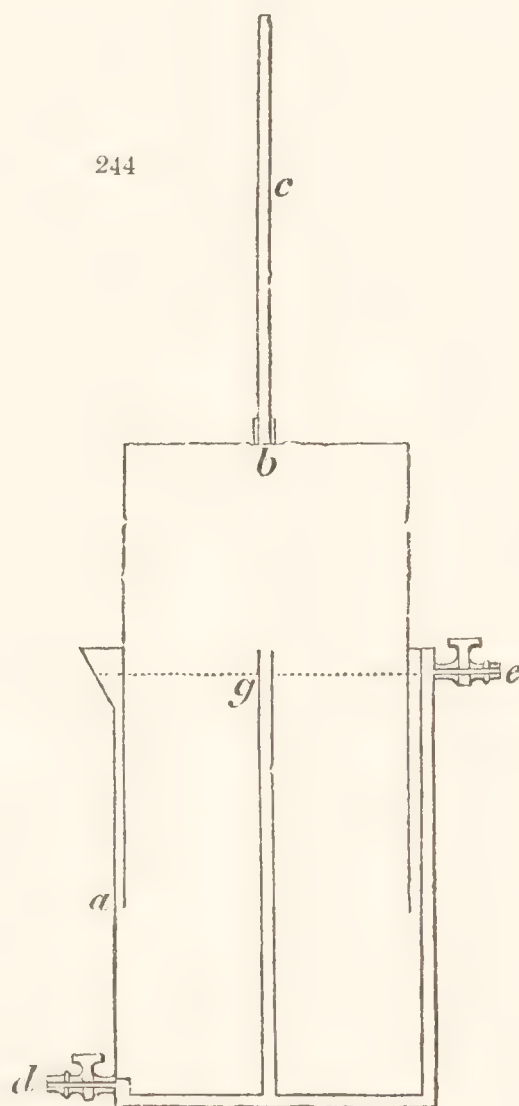
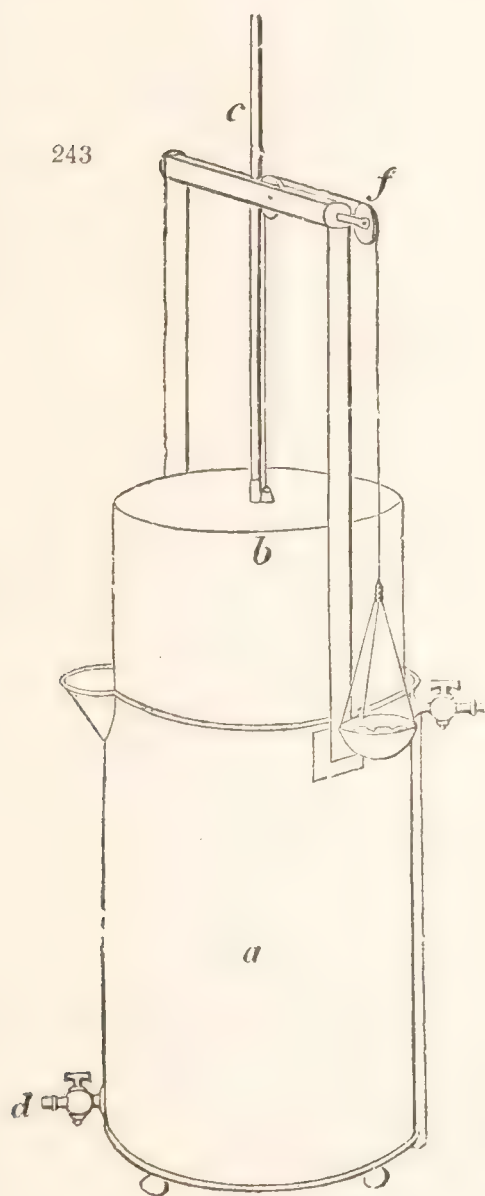


may hold from two to six or eight gallons: *b*, is a cistern from which issue two tubes, supplied with stop-cocks, one entering the reservoir at its upper part, the other continued, as shown by the dotted lines, to near the bottom: *c*, is a short tube issuing from the bottom of the reservoir, and capable of being accurately closed by a screw. *d*, is a glass tube communicating at both ends with the body of the gasholder. When it is intended to fill this apparatus with gas, the tube *c* is closed, and the stop-cocks, *e*, *f*, are opened; water is then poured into the cistern, which, running down the long tube *e*, forces the air out through the shorter one *f*. The reservoir being thus filled, the stop-cocks are closed, and the aperture *c* is opened, into which

the beak of the retort, or tube, whence the gas issues, is introduced, and, bubbling up, displaces the water, which runs out at the same opening. When it is seen in the tube, *d*, that nearly the whole of the water is displaced, the aperture *c* is closed; the vessel is now filled with gas, which may either be drawn off into receivers, placed in the water-cistern *b*, by opening the two stop-cocks *e*, *f*; or by closing the stop-cock, *f*, and opening *g*, it may be propelled into bladders, or transferred in any convenient way by an attached tube.

A view and section of the *gasometer* are shown in the following sketches (figs. 243, 244): it may be made of japanned or zincd iron or copper. *a*, is the outer circular vessel, or pail, to the sides of which the tubes *d*, *e*, (each fitted with a stop-cock externally,) are soldered. The tube *d* passes along the bottom of the pail, and proceeds to the centre, where it joins the tube *e*, which commences at the top of the pail at the

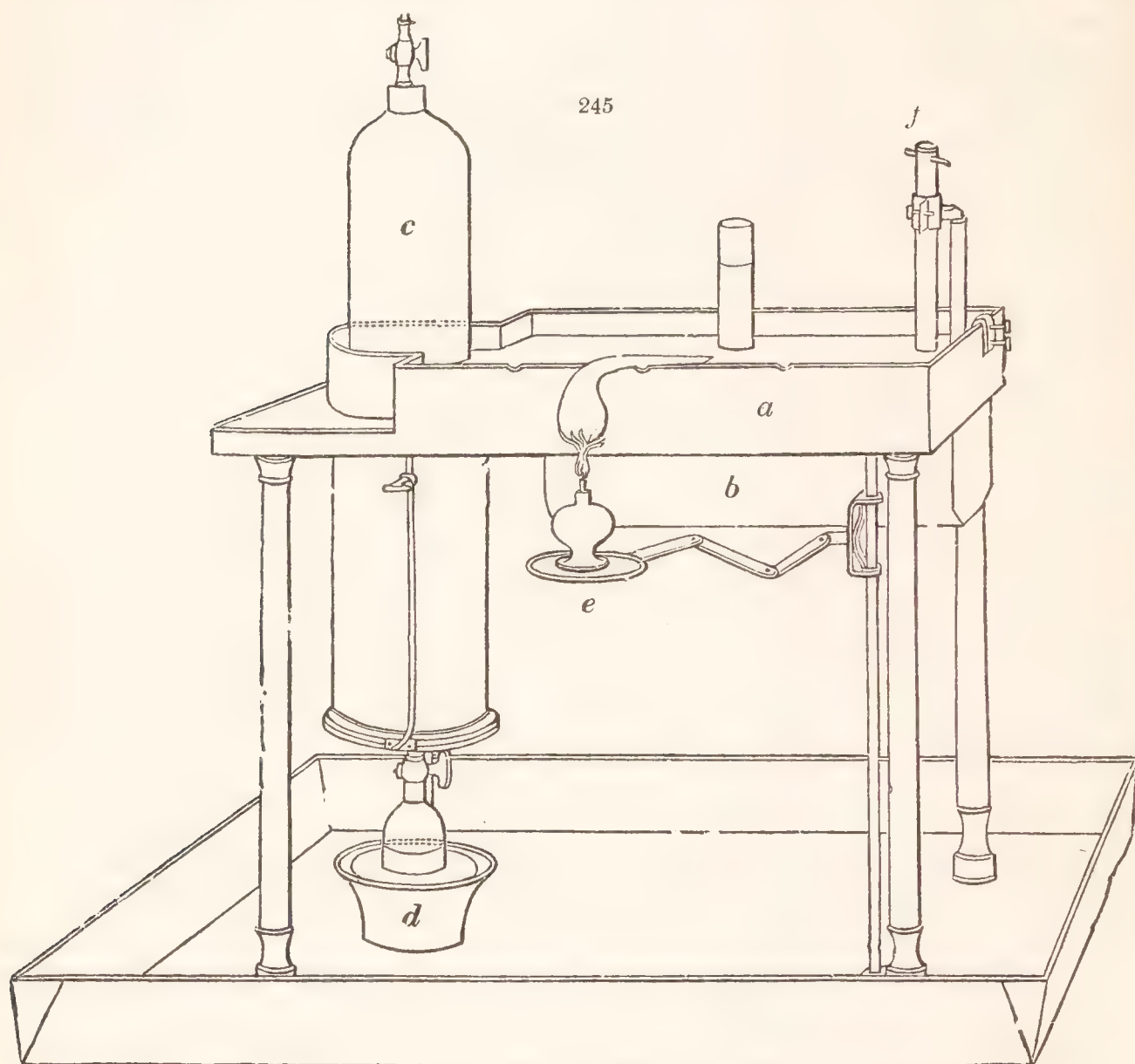
cock *e*, and proceeds downwards; and, from the place of junction, the upright tube *g* rises through the middle of the pail, a little above the level of its upper rim. The vessel *b* is a cylinder open only at bottom, and of less diameter than the pail in which it is inverted, and can move up and down freely. This cylinder has a solid stem *c*, which passes through a hole in the cross-bar of the frame fixed to the top of the pail; it serves to steady the cylinder, and to indicate the quantity of the inclosed gas: the weight of the cylinder is counterpoised in any convenient way; generally by a weight and cord passing over the pulley *f*.



To use this gasometer, first let the cylinder fall to the bottom of the pail and fill the latter with water; then shut the cock *e*, and open *d*, and connect it with the tube which conveys the gas from the retort, gasholder, or other vessel; or, if more convenient, shut *d*, and convey the gas through *e*. The gas rises, and gradually lifts up the cylinder, which must be properly balanced: and when sufficiently filled, the cock, by which it entered, must be closed. The gas may now be drawn off at either of the stop-cocks, by a tube passing into the water-trough, or it may be propelled through a blow-pipe, or otherwise employed.

Those gases which are absorbed by water may, in most instances, be collected over mercury. The best form of the *Mercurio-pneumatic apparatus* is that contrived by Newman. (*Quarterly Journal*, i., 185.) It is a

trough of cast-iron, supported by brass or iron legs, and having a small gasometer at one end. It is placed in a japanned iron tray to collect the scattered mercury, as shown in the wood-cut (fig. 245). *a* is the shallow,

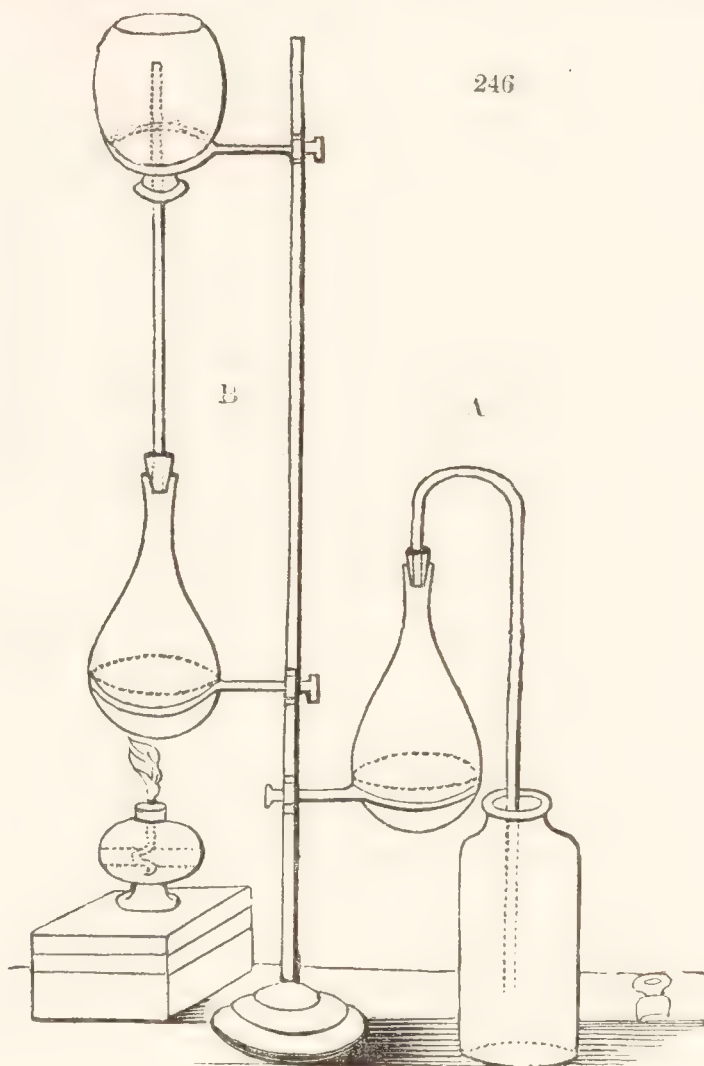


b the deeper part of the trough; *c* is a small mercurial gasometer connected with it, filled from the bottom through the small basin of mercury at *d*; *e* is a sliding stand for a lamp, *f* a detonating tube screwed into a spring support. The gas-jars and receivers used over the mercurial trough should be of thicker glass, and therefore stronger and heavier than those which suffice in the water-apparatus, and the trough should always stand, as above represented, in a japanned iron tray, and should have a cover to keep out dirt and dust when not in actual use.

It frequently happens that a mercurial pneumatic trough, upon a much smaller scale than the above, is sufficient for mere experiments of research; and, in that case, it is either made of porcelain, or of cast-iron, or wood, being hollowed out of a block of mahogany. The larger trough, as usually constructed, requires not less than from seventy to eighty pounds of mercury for the convenient performance of experiments, but the smaller mercurial troughs may be used with only from twenty to thirty pounds of mercury: these also should stand in proper trays to prevent the loss of the spilt mercury.

The chemical lecturer may in many instances altogether dispense with

the trouble and expense of a mercurial bath, by collecting gases in dry glass vessels, especially when he requires very large jars or bottles to be filled with gas, and at the same time kept *dry*, but where a small admixture of atmospheric air is unimportant. For this purpose, the materials producing the gases are introduced into a flask furnished with a tube of convenient length, and twice bent at right angles, so as to pass to the bottom of a clean stoppered phial: the disengaged gas, if heavier than the air, displaces it; when it is full, it must be cautiously withdrawn, and stopped, and another phial put into its place: (fig. 246) A. If the gas thus to be collected is lighter than the atmosphere, the tube from the flask may be straight, and pass up into an inverted phial, as at B.



§ I. OXYGEN. O. 8.

THIS elementary body was discovered by Priestley on the 1st of August, 1774; he called it *dephlogisticated air*; it was termed *empyreal air* by Scheele, and *vital air* by Condorcet. The name *oxygen* was given to it by the French nomenclaturists, implying its tendency to form *acid* compounds (from $\acute{o}\xi\acute{\upsilon}\varsigma$, *acid*, and $\gamma\epsilon\nu\nu\epsilon\acute{\iota}\nu$, to *generate*). It is more abundantly diffused throughout nature than any of the other elementary bodies; it forms eight-ninths of the weight of water, about one-fifth of the weight of the atmosphere, and a large relative proportion of the mineral bodies which form the solid matter of the globe. It also constitutes, with scarcely one exception, an element of the various products of organized bodies both animal and vegetable.

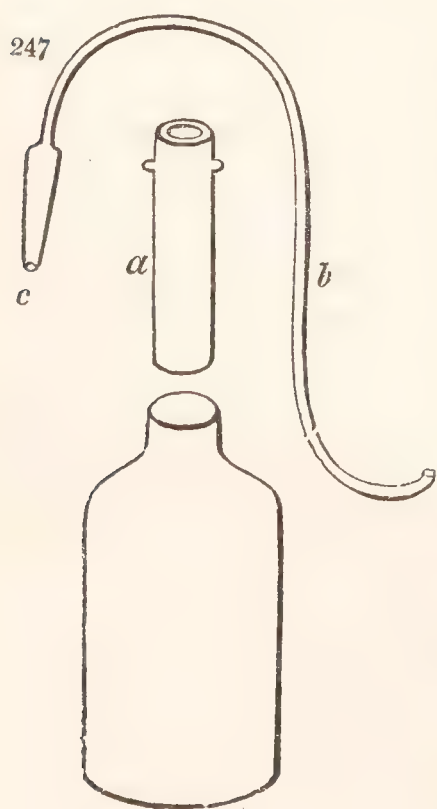
Oxygen gas may be procured by a variety of processes, of which those only in common use will be noticed here, and others adverted to in their proper places.

To obtain oxygen in the purest state, proceed as follows: introduce into a small glass *retort* (as shown at D, fig. 236,) about 100 grains of the salt called *chlorate of potassa*, and gradually heat it over a gentle charcoal fire, or by means of a large spirit-lamp, having previously placed the beak of the retort under the shelf of the hydro-pneumatic apparatus. Suffer the common air of the retort to escape, and when the salt fuses and appears to boil, collect the oxygen which it then gives

out, in proper vessels, taking care so to adjust the heat as to cause the gradual decomposition of the salt, and occasion the air-bubbles to follow each other with moderate rapidity, especially towards the end of the process, when a torrent of gas is apt to be rather suddenly evolved, in consequence of the formation of a portion of perchlorate of potassa, which is decomposed at that period. At last the heat may be so far increased as to render the bottom of the retort red-hot, being careful however, not to fuse it; when gas ceases to be evolved, withdraw the retort and put it aside: it is, however, seldom fit for a second operation. From 100 grains of the chlorate, we may expect to obtain nearly 100 cubic inches of gas. (The proximate elements of chlorate of potassa are potassa, KO, and chloric acid, ClO₅: the effect of heat is to convert the salt into *chloride of potassium*, which remains in the retort, and *oxygen gas*, which is evolved: KO, ClO₅ becoming KCl, + O₆.)

The addition of a few small particles of binoxide of manganese to the chlorate of potassa causes it to yield up its oxygen much more readily and at a lower temperature, so that the heat of a common spirit-lamp is quite adequate to its evolution: this mutual reaction is attended by such elevation of temperature that the oxide becomes red-hot. (DÖBEREINER.) Oxide of copper may be substituted for that of manganese. (MITSCHERLICH, *Ann. Ch. et Ph.*, January, 1843, p. 7.) These are cases of what has been termed *catalytic action*, for the metallic oxides themselves are not necessarily affected, but apparently facilitate the decomposition by mere *presence or contact*.

Another substance from which oxygen may be obtained, and probably at a somewhat cheaper rate, is *black oxide of manganese*, but the gas derived from this source is never perfectly pure, and the quantity produced from a given weight of the oxide is liable to much variation. A pound should yield from 40 to 50 pint measures. (11 ounces troy will give 1 ounce, or 1387 cubic inches. THOMSON. 1 ounce yields, if quite pure, 128 cubic inches. TURNER. 1 pound troy gives about 700 grains, or nearly 2000 cubic inches, equal to 7 imperial gallons. KANE.) The oxide of manganese should be coarsely powdered, dried, and introduced into an iron gas bottle, which may be about four fifths filled with it, and placed with its proper connecting tubes, in a convenient furnace or fire-place*. These bottles should be made of wrought iron, of the shape annexed (fig. 247), their capacity being from one to three pints. The connecting tube *a* should be of iron, and fitted by grinding it into the neck of the bottle; and the delivery tube *b*, which may be of pewter,



* The oxide of manganese is sometimes mixed with portions of the *hydrated oxide*, in which case the steam evolved at a high temperature is very troublesome. When purchased in fine powder, carbonaceous matter is sometimes present, and the oxygen is, in that case, contaminated by carbonic acid.

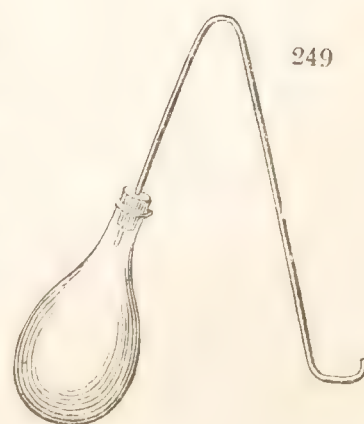
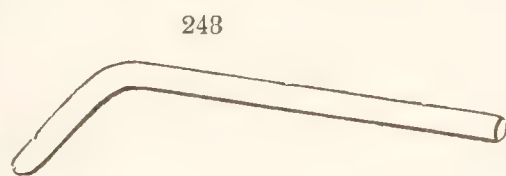
with a brass or copper piece soldered on to it at its conical end *c*, should be similarly ground into the upper end of the connector. When these bottles are used, the joints may be made tight by the previous application of a little grease. The wrought-iron bottles, in which mercury is usually imported, answer very well as gas-bottles; but in all common cases their size is inconveniently large.

When the oxide of manganese becomes red-hot, the oxygen begins to escape by the pewter tube, which must be so bent as to pass under the shelf of the water apparatus. Collect some of the gas in a small jar or tube, and test it by introducing into it a slip of wood which has been inflamed and blown out, so that the end remains only glowing; if the gas be sufficiently pure, the glowing wood will immediately burst into flame and burn vehemently: the oxygen may then be collected for use, either in bottles, jars, gasholders, or gasometers, as required. When the gas ceases to be evolved, the bottle must be removed from the fire; and, when cold, emptied of its contents, which will be found to be an oxide of manganese, of a brown colour, containing of course less oxygen than the black, and not further decomposable by heat alone, except at an extremely high temperature. (2 equivalents or 88 parts by weight of binoxide of manganese yield 1 equivalent or 8 parts by weight of oxygen and 1 of sesquioxide of manganese, as in the following equation: $2 \text{MnO}_2 = \text{Mn}_2\text{O}_3 + \text{O}_2$.)

Oxygen gas may also be obtained from a mixture of pulverised black oxide of manganese and sulphuric acid, in such proportions as to be about the thickness of cream; this mixture is put into a glass retort, and heated over an Argand lamp, the gas being collected in the usual way. (In this case, 1 equivalent of binoxide and 1 of sulphuric acid yield 1 equivalent of protosulphate of manganese and 1 of oxygen. $\text{MnO}_2 + \text{SO}_3 = \text{MnO}, \text{SO}_3 + \text{O}_2$.) This method is sometimes convenient where an iron retort cannot be procured; but is not economical, and the ingredients are apt to harden in the retort, which is often broken in attempting to cleanse it. When a mixture of bichromate of potassa and sulphuric acid is heated, oxygen also is evolved.

If perfectly pure oxygen be required, it must not only be obtained from chlorate of potassa, but also collected over mercury; and as it is often wanted in the experimental laboratory in very small quantities only, a tube-retort, made of green or plate-glass, bent into the annexed form (fig. 248), may be conveniently used, or a small flask with a bent tube fitted to it, as in fig. 249.

It must also be recollected, in all delicate experiments with oxygen and other gases, that they retain, as usually procured, more or less vapor of water, so that to obtain them *dry*, it is necessary to convey them through tubes over substances which will abstract the watery vapor which they contain, without in any way affecting the purity of the gas itself. Oxygen may thus be dried by passing it through a long tube containing fragments of fused *chloride of calcium*;



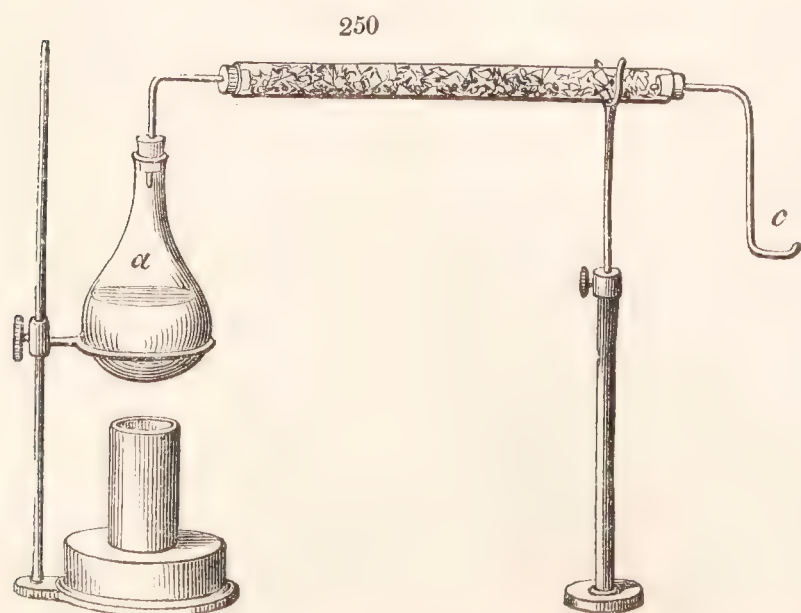
sulphuric acid, fused potassa, and some other substances, are also occasionally used for the same purpose*.

Oxygen gas is insipid, colorless, and inodorous; it is permanently elastic, under all known pressures and temperatures. Its specific gravity compared with air, is as 1.1093 to 1.000. Compared with hydrogen, its specific gravity is = 16, hydrogen being = 1. At mean temperature and pressure, 100 cubic inches weigh 34.38 grains: or according to Thomson, 36.43 grains at the temperature of 32°. According to Dulong and Berzelius, the specific gravity of oxygen is 1.1026, and 100 cubic inches weigh 34.109 grains (*Ann. Ch. et Ph.*, xv. 386); according to Davy, its specific gravity is 1.127; according to Thomson, 1.1111. Its refractive power, in regard to light, is less than that of any known body: compared in this respect with atmospheric air, it is as 0.830 to 1.000. According to De la Roche and Berard, its specific heat, compared with an equal *volume* of air, is = 0.9765, and with an equal *weight* of air, = 0.8848, that of air being = 1.000. It is evolved by electrolytic action at the positive electrode, or anode, and therefore stands among the electro-negative bodies, or anions, as defined by Faraday. (p. 221.)

When powerfully compressed by the sudden depression of a piston in a glass tube, oxygen appears to become momentarily luminous, a property which has been considered as one of its characteristics. Thenard, however, has shown that this appearance is connected with the presence of grease or oil upon the compressing piston, and that the gas, although much heated by sudden compression, is not of itself luminous.

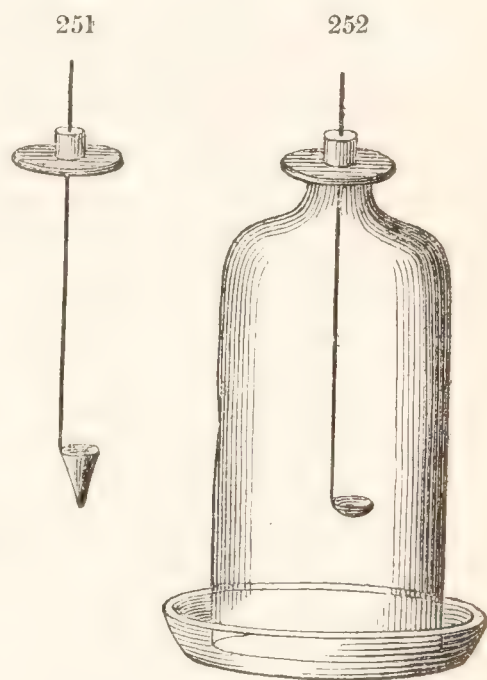
It is absorbed in very small quantity only by water: 100 cubic inches of water, freed from air, taking up not more than 3.5 cubic inches of oxygen. (HENRY, *Phil. Trans.*, 1804, p. 174.) It does not alter the color of litmus, nor does it render lime-water turbid.

It is a powerful supporter of respiration. A small animal, confined in oxygen gas, lives about thrice as long as when confined in the same bulk of common air; it has, therefore, been called *vital air*; but we are not thence to conclude that it is fit for the continuous support of life: on the contrary, an animal made to breathe oxygen for any length of time, falls a sacrifice to excess of arterial action, and after death the blood in the veins is found as florid as that in the arteries.



* Where gas requires to be dried, the following form of apparatus is generally used. *a* is the flask in which the gas is generated, *b* a tube loosely filled with small fragments of fused chloride of calcium, and *c* the tube conveying the gas into the mercurial trough. Fused potassa is sometimes substituted for the chloride of calcium, where the latter absorbs or otherwise affects the gas passed over it; and when oil of vitriol is used, the tube is usually bent into the shape of the letter U, and filled with fragments of pumice moistened with the acid.

Oxygen eminently *supports combustion*. A lighted taper, introduced into this gas, is very rapidly consumed, with intense ignition and enlargement of the flame; and if it be previously blown out, so that the wick continues glowing (and for such experiments pieces of *green* wax-taper answer best), it immediately bursts into flame when plunged into the jar of oxygen. Sulphur, which burns in the air with a small blue flame, has its flame enlarged when immersed in a jar of oxygen, and blazes with a beautiful purple color, dissolving as it were in the oxygen, and converting it into sulphurous acid gas, which is absorbed by water. Phosphorus, when inflamed in the atmosphere, burns with a bright light, but in oxygen the eye can scarcely bear its brilliancy, and the heat which it evolves is very intense: a piece not larger than a pea should be used in the experiment. The oxygen combines with the phosphorus, and forms a quantity of white flaky matter, very soluble and deliquescent, which is chiefly phosphoric acid. This, and the combustion of sulphur, may be best performed by placing them in a small copper spoon or cup, attached to a wire annexed to a spare stopper, or passing through a brass collar, or a cork which fits the neck of the air-jar. The disadvantage of a cork is, that it is sometimes apt itself to take fire and crack the jar, the most convenient arrangement consisting in a copper spoon or cup attached to a copper wire sliding through a collar in a ground brass disc which lies upon the ground neck of the air-jar: the small spoon or capsule is often a convenient shape, but for combustion in oxygen, where, as in the case of phosphorus, the action is very intense, and the fused combustible liable to drop, a small conical receptacle is preferable; these arrangements are represented in figs. 251 and 252.



One of the most brilliant instances of combustion in oxygen is the burning of iron wire. For this purpose the jar should be capacious, and placed over water in a common soup plate; the oxygen should be very pure. A piece of thickish annealed iron wire should be attached to the spare stopper, and loosely wound round with repeated twists of harpsichord wire, so as to form a tangled coil; the sulphur tip of a match should then be broken off, and affixed to the end of it; when this is inflamed, and the coil immersed into the jar of gas, vivid combustion soon ensues: it throws off brilliant sparks, and partly fuses into globules of oxide, which falling through the water, lie for some time red-hot upon the plate, and often fuse it at the point of contact. A piece of annealed watch-spring, a thin file, or long shavings which may be obtained from the turners of steel or iron, may also be used for this experiment.

In these cases of combustion in oxygen gas, the sudden expansions which take place are apt to endanger the bell-glass, which should, therefore, if necessary, be held by the hand, so as to allow the occasional escape of a little of the gas, and at the same time prevent its jarring upon the plate beneath.

The results of the above, and other cases of combustion in oxygen, will be more fully detailed and explained hereafter. (See *Carbon, Sulphur, Phosphorus, and Iron.*) It may suffice to state at present, that in all cases of combustion in oxygen, the combustible and the oxygen combine, and the product of combustion consequently manifests an increase in weight proportionate to the quantity of oxygen with which it has united. *Acids* and *oxides* will be found to be the result of these combinations, which are either effected slowly, and without sensible evolution of heat and light; or rapidly, with the phenomena of combustion and flame: or with intermediate rapidity, exciting considerable elevation of temperature, and often even a red-heat, though without flame, as in some cases which have been already cited (p. 129.)

The terms *oxidizement* and *oxidation* imply the combination of oxygen with bodies; and its abstraction or separation is *deoxidizement* or *reduction*. All the elementary substances are susceptible of oxidizement, and most of them, at certain temperatures, with the evolution of heat and light; these are in common language termed *combustible* or *inflammable bodies*; when a substance is saturated with oxygen, it becomes *incombustible*; that is, incapable of entering into further combination with it. Bodies saturated with the other supporters of combustion are also incombustible, hence the perchlorides, periodides, &c., come usually under that definition. All *organic* bodies are combustible.

The *phenomena of combustion* were referred by Stahl and his associates to a peculiar principle which they called *phlogiston*; it was supposed to exist in all combustibles, and combustion was said to depend upon its separation: but this explanation, though apparently supported by experimental evidence, was at variance with the well-known fact, that bodies during combustion increase in weight.

After the discovery of oxygen gas, it was adopted by Lavoisier as the universal supporter of combustion. The ponderable basis of the gas was supposed to unite to the combustible, and the heat and light which it before contained in the gaseous state, were said to be evolved in the form of flame. But in this hypothesis several requisites are not fulfilled; the light depends upon the combustible, and not upon the quantity of oxygen consumed; and there are numerous instances of combustion in which oxygen, instead of being solidified, becomes gaseous during the operation; so that the theory of latent heat is insufficient; and, lastly, in others, no oxygen whatever is present. Combustion, therefore, cannot be regarded as dependent upon any peculiar principle, or form of matter, but must be considered as a general result of intense chemical action. It may be connected with the electrical energies of bodies; for all bodies which powerfully act upon each other are in the opposite electrical states of positive and negative; and the evolution of heat and light may depend upon the annihilation of these opposite states, which happens whenever they combine.—See the Section on *Electricity*; and the article *Atmospheric Air*.

It appears, from the researches of Despretz, that the *heat* evolved in all common cases of combustion depends, not upon the combustible, but upon the quantity of oxygen consumed: thus, a pound of oxygen, in combining respectively with hydrogen, charcoal, alcohol, and ether, evolved in each case very nearly the same quantity of heat, each raising

29 pounds of water from 32° to 212°. With respect to the comparative quantities of heat evolved by a given weight of different combustibles, he obtained the following results:—

1 pound of pure charcoal raised	78 pounds of water from 32° to 212°
„ common wood charcoal	75 „ „ „
„ baked wood.....	36 „ „ „
„ wood holding 20 per cent. of water	27 „ „ „
„ bituminous coal	60 „ „ „
„ turf..... 25 to	30 „ „ „
„ alcohol.....	68 „ „ „
„ oil, wax	90 „ „ „
„ ether	80 „ „ „
„ hydrogen	236 „ „ „

The evolution of *light*, as a result of combustion, has already been noticed, and also the phenomena of combustion and oxidizement at comparatively low temperatures. All cases of oxidizement are probably attended with the evolution of heat, but where the process is slow, the evolved heat is unobserved and dissipated without accumulation: in other cases, where the process is effected in a shorter period, the heat becomes proportionably sensible; and where the oxidizement is rapid, the whole of the heat being evolved in a much more limited time, is proportionably exalted in intensity. A pound of charcoal, for instance, combining with oxygen in the process of respiration, evolves the same absolute amount of heat as when in a state of ignition, and combines with the same quantity of oxygen; but in the former case, the combustion, so to say, is spread over thirty hours, and in the latter may be effected in as many minutes.

§ II. CHLORINE. Cl. 36.

CHLORINE was discovered by Scheele in 1774. Consistently with the theoretical notions of its nature, he called it *dephlogisticated muriatic acid*. (*Mem. Acad. Stockholm*, 1774, p. 94.) The term *oxymuriatic acid* was afterwards applied to it by the French chemists. (BERTHOLLET, *Jour. de Phys.*) The more appropriate term *chlorine*, (from $\chi\lambda\omega\rho\acute{o}s$, *green*,) which merely designates its greenish-yellow color, was given to it by Davy, who, in 1810, published a masterly essay on its nature, (in the *Phil. Trans.*,) showing that so far from containing loosely-combined oxygen, as had been suspected, that element could not be proved to exist as one of its component parts; also that it contained no muriatic acid; that in all cases of the *apparent* evolution of oxygen and muriatic acid from chlorine, water was present, and was decomposed; and that, in the present state of our knowledge, chlorine must be regarded as an uncompounded or elementary body. Its great natural source is sea-salt, or *chloride of sodium*: it also occurs in several other combinations.

To obtain chlorine, a mixture of one part by weight of coarsely powdered black oxide of manganese and two parts of common hydrochloric acid may be heated over a lamp in a glass retort. (1 atom of binoxide of manganese and 2 of hydrochloric acid yield 1 of protochloride of manganese, 2 of water, and 1 of chlorine. $MnO_2 + 2 HCl = MnCl + 2 HO + Cl$. See HYDROCHLORIC ACID.) Chlorine is soon copiously evolved, and may be conveniently collected over warm water; it is

absorbed by cold water, and cannot, therefore, be long retained over that fluid; so that it should be received into bottles provided with ground stoppers: when these are full, the stopper, previously greased a little, should be introduced under water, care being taken to exclude the water from their interiors. In consequence of the deleterious nature of chlorine, its escape into the atmosphere of the laboratory should be prevented, by collecting the first portions which come over mixed with the common air of the retort, in a jar, which may afterwards be carried away into the open air, or placed under a chimney. The gas may be preserved for use when it passes over of its full color, to judge of which, the neck of the retort should be kept clean; the retort should not be more than half filled with the materials, which are otherwise apt to boil over, and soil the water in the trough.

When chlorine is required perfectly pure and free from hygrometric moisture, it should be first passed through water, and afterwards conducted through a tube containing fragments of fused chloride of calcium, and ultimately into a clean dry bottle, from which it will expel the atmospheric air, as explained by fig. 246; it cannot be collected over mercury, as it immediately combines with that metal.

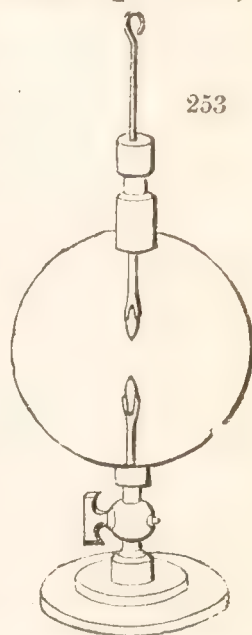
Chlorine may also be procured from a mixture of 8 parts of common salt, 3 of pulverized black oxide of manganese, 4 of water, and 5 of sulphuric acid: or the proportions recommended by Thenard may be used; viz., 4 parts of common salt, 1 part of oxide of manganese, 2 of sulphuric acid, and 2 of water. The theory of its production in these cases will be explained afterwards. See *Hydrochloric Acid* and *Sulphate of Soda*.

Chlorine, at common temperatures and pressures, is a gaseous fluid, which, when perfectly dry, suffers no change by exposure to a temperature much below 0° ; but, in its ordinary state, it generally contains aqueous vapor, which, at a temperature of 32° , is deposited in combination with chlorine, in the form of a white crystalline compound, which liquifies, effervesces, and is again taken up by the gas, upon the application of heat. This *hydrate of chlorine* may be best obtained by introducing into a clean bottle of the gas a little water, and keeping it for a few days in a dark place, at a temperature not exceeding 32° . It then forms prismatic and acicular crystals, having a specific gravity of about 1.2, and composed of 27.7 chlorine and 72.3 water, or about 1 atom of chlorine to 10 of water. (FARADAY. *Quarterly Journal*, xv.)

Chlorine was the first of the gases supposed to be permanently elastic which Faraday succeeded in condensing into the liquid state: he effected this by putting some of the hydrate of chlorine into a small bent tube, hermetically sealed, and applying a gentle heat; a yellow vapor formed, which condensed in the cold part of the tube into two distinct fluids, the uppermost and lightest of which was mere aqueous solution of chlorine, but the heavier was yellow, and separable by careful distillation. If, when the fluids were separated, the tube was cut in the middle, the parts flew asunder with an explosion, the whole of the yellow portion disappeared, and gaseous chlorine was produced. When the end of the tube containing the yellow fluid was broken under water, there was also an immediate escape of gaseous chlorine. The specific gravity of chlorine, when condensed into the liquid form, is about 1.33. It is a non-con-

ductor of electricity; its refractive power is rather less than that of water. (*Phil. Trans.*, 1823, p. 160.) It does not freeze at the very low temperature of 166° below 0° Fahrenheit. (FARADAY. *Phil. Trans.*, 1845, p. 170.)

When gaseous chlorine is dry and pure, it is not affected by light, neither is it altered by high temperatures. Davy exposed it to the continued action of charcoal intensely ignited by voltaic electricity, without the smallest change in its properties. The apparatus which he used consisted of a glass globe (fig. 253), having at its upper part a sliding wire passing air-tight through a ground collar, to the lower end of which was attached a piece of well-burned charcoal: at bottom was a stop-cock supporting a pincers, holding another pointed piece of charcoal; the globe was exhausted, filled with chlorine, and the stop-cock and sliding wire were connected with the extremes of a powerful voltaic battery, so as to maintain the charcoal points in a state of intense ignition.



Chlorine gas is of a greenish-yellow color, a pungent and disagreeable smell, a peculiar and somewhat astringent taste, highly irritating and injurious when respired, and exciting cough and great irritation of the lungs, and mucous secretion from the trachea and bronchiæ, even when considerably diluted with atmospheric air. In some pulmonary complaints, the respiration of air slightly tainted by the admixture of chlorine has been resorted to as a stimulant. "It is not a little remarkable, that chlorine, if very much diluted, although still apt to excite cough, is found to alleviate the symptoms of ptysis when inhaled, probably by promoting expectoration: the patients themselves soon learn to bear it stronger, and to long for the hour of inhaling it. It is also stated that the workers in manufactories of bleaching powder, and in bleaching and dye works, where the air is always to some extent charged with chlorine, are less liable to ptysis than others; so that up to a certain point the system seems capable of becoming habituated to it with benefit." GREGORY.

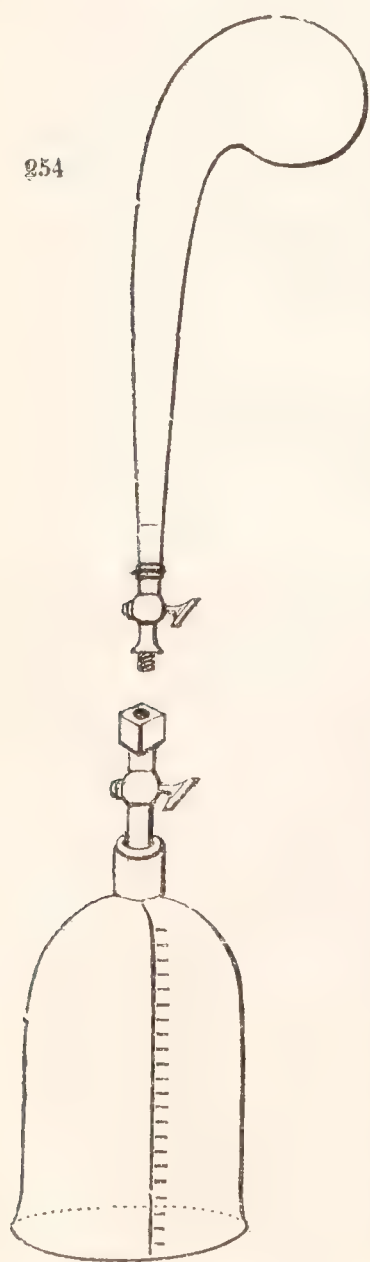
The specific gravity of chlorine compared with air is, according to Gay Lussac and Thenard, 2.470, which gives 76.59 grains as the weight of 100 cubical inches at mean temperature and pressure. According to Davy, its specific gravity is 2.395, and 100 cubic inches weigh between 76 and 77 grains. According to Thomson, the specific gravity of chlorine is 2.5, and at the temperature of 32° 100 cubic inches weigh 81.975 grains. Its specific gravity, in reference to hydrogen, may be considered as 36 to 1. Its atomic weight is 36. (35.42 BERZELIUS. 35.84 TURNER.) Chlorine is an electrolytic anion.

At the temperature of 60° , water dissolves twice its volume of chlorine. The solution, saturated at 42° , has a specific gravity of 1.003; it is of a pale yellow color, has an astringent, nauseous taste, and destroys vegetable colors: hence its use in bleaching: though chlorine itself, when perfectly free from moisture, has scarcely any such action. Hence the bleaching agency has been by some regarded as due to the evolution of nascent oxygen resulting from the decomposition of water.

The aqueous solution of chlorine freezes at 32° , forming the crystalline hydrate above mentioned, and ice which is free from chlorine. (FARADAY.)

When this solution is exposed to the direct rays of the sun, oxygen is evolved in consequence of the decomposition of the water, the hydrogen of which unites to the chlorine, and forms hydrochloric acid. The same change ensues more slowly in common day-light, but in the dark there is no such decomposition; so that as gaseous chlorine generally contains aqueous vapor, the bottles in which it is preserved should be excluded from light.

Chlorine, and its aqueous solution, are powerful antiseptics, and destroyers of contagious and infectious matter, and of bad odors. This property depends on the power which chlorine has of decomposing those noxious compounds, and resolving them into others which are harmless. For the purposes of fumigation, chlorine liberated from black oxide of manganese and hydrochloric acid, or from manganese, salt, and sulphuric acid, may be diffused through the atmosphere of the infected chambers; or the infected goods may be exposed to it. In the same way the offensive odors of dead bodies may be mitigated by sprinkling them with solution of chlorine. (See *Chloride of Soda*, *Chloride of Lime*, &c.) When it is wished to fumigate with chlorine, saucers containing the mixture which evolves it should be placed in the higher parts of the room, as it then descends on account of its density, and becomes sooner blended with the surrounding air.



When a burning taper is immersed in a jar of chlorine, the brilliancy of the flame is much impaired; it becomes red, throws off dense fumes, and is soon extinguished. There are, however, many bodies, such as phosphorus and several of the metals, which are spontaneously ignited by chlorine, and burn in it with much energy. In these cases, binary compounds result, some of which, like those of oxygen, are possessed of acid properties: others are not acid, and are termed *chlorides*. Brass or copper leaf, and powdered antimony, serve well to show the intense action of chlorine upon certain metals. When introduced into the gas, they enter into immediate combustion, and *chloride of copper* and *chloride of antimony* are formed. The best way of making these experiments consists in introducing the phosphorus, or the copper leaf, into a retort, mounted with a stop-cock, and exhausted upon the air-pump; it is then screwed into the cap of an air-jar of chlorine, also mounted with a stop-cock, and standing over water (fig. 254). Upon opening the cocks, the gas rushes into the retort, and the phosphorus or copper leaf immediately burns. In consequence of their irregular thickness and form, retorts are frequently broken by the air's pressure whilst exhausting; so that it is safe to cover them with a cloth during the process, to prevent the splinters being thrown about. A

piece of bibulous paper, imbued with oil of turpentine, is also spontaneously inflamed when put into a jar of chlorine.

The presence of chlorine is recognized by its bleaching power, by its odor and color, and by its action upon solution of nitrate of silver, in which it occasions a white curdy precipitate, insoluble in nitric acid, but soluble in liquid ammonia, and speedily blackening by exposure to light. It is also detected by electrolytic action, as already shown (p. 222).

CHLORINE AND OXYGEN. No compound of these two elementary substances can be obtained by their direct mutual action, for they have but a feeble affinity for each other, and, when combined, are easily separable. By presenting chlorine and oxygen, however, to each other, under certain conditions, they form four distinct compounds, namely,

1. Protoxide of chlorine, or hypochlorous acid (chlorous acid) = ClO or Cl_2O_2 .
2. Peroxide of chlorine, or hypochloric acid..... = ClO_4 .
3. Chloric acid = ClO_5 .
4. Perchloric acid = ClO_7 .

PROTOXIDE OF CHLORINE. HYPOCHLOROUS ACID (of Balard) = Cl_2O_2 . **CHLOROUS ACID** (of Gay Lussac) = ClO . In the *Phil. Trans.* for 1811, Davy has described a peculiar gas, to which, on account of its deep yellow-green color, he gave the name of *Euchlorine**. He obtained it by mixing in a small retort, 2 parts of chlorate of potassa with 1 of water and 1 of hydrochloric acid, and applying a *very gentle heat*, so as to cause a moderate effervescence: he collected it in small jars or tubes over mercury; but the best way of examining it is to retain it in the tube or vessel in which it is generated, or to collect it by displacement in a clean dry phial or jar.

This gas has a peculiar odor, like diluted chlorine, and is pernicious to respiration. Davy found its specific gravity to vary; he estimated it at about 2.4: Gay Lussac and Thenard regard it as = 3. Water dissolves ten volumes of this gas, and acquires its peculiar odor, and a yellow color; it destroys most vegetable colors, previously reddening some of the blues. Its most remarkable character is the facility with which it is decomposed: when gently heated in the upper part of a small tube standing over mercury, a kind of explosion, attended by a flash of light, ensues, and the tube is projected to some distance; but if it be firmly held down in the mercury, the results of the decomposition are retained. According to Davy, 50 volumes are thus expanded to 60, consisting of a mixture of 40 of chlorine and 20 of oxygen: according to Gay Lussac, 2 volumes become 3, composed of 2 volumes of chlorine and 1 of oxygen. According to this view *protoxide of chlorine* would consist of

						Gay Lussac.	
						Volumes.	S. G.
Chlorine	1	...	36	...	81.82	1.0	2.45
Oxygen	1	...	8	...	18.18	0.5	0.55
	<u>1</u>		<u>44</u>		<u>100.00</u>	<u>1</u>	<u>3.00</u>

This gas sometimes explodes whilst it is collecting, or in being transferred from one vessel to another, or even by the heat of the hand; so that it should be cautiously dealt with and examined, and collected in small quantities only. Detonated with hydrogen, in the proportion of 5 measures of the gas to 8 of hydrogen, it gives rise to the produc-

* It would appear probable from the recent experiments of Gay Lussac, that the color of this gas is to be ascribed to the presence of peroxide of chlorine.

tion of water and hydrochloric acid. It is decomposed by all burning bodies, and their combustion continues as it would in a mixture of chlorine and oxygen in the above-mentioned proportions. A small piece of phosphorus let up into the gas instantly takes fire and absorbs it, burning with much brilliancy.

The experiments of Soubeiran (*Ann. Ch. et Ph.*, xlviii. 113) rendered it probable that euchlorine was a mixture of chlorine with peroxide of chlorine, an opinion which some of Davy's observations seemed to corroborate; the more recent researches, however, of Balard and of Gay Lussac, have much extended our knowledge of the nature and properties of this body. Balard, in a valuable paper on the bleaching compounds of chlorine, (*Ann. Ch. et Ph.*, lvii. 225,) has shown the mode of obtaining it in a pure form; he calls it *hypochlorous acid*. His process consists in agitating a mixture of one part of precipitated red oxide of mercury with twelve of distilled water, in a bottle filled with chlorine; the gas is rapidly absorbed: if the proportion of the oxide is insufficient the deposited powder is white, and some of the chlorine remains unabsorbed; but the oxide should be in slight excess, so as to remain red, and entirely absorb the gas; (6 drachms of red oxide mixed in fine powder with an ounce and a half of water, and shaken in a quart bottle of chlorine, are the proportions recommended by Graham.) When the absorption is complete, the contents of the bottle are poured upon a filter, and the filtrated liquor subjected to distillation in vacuo, by which a diluted solution of hypochlorous acid is obtained, and which may be concentrated by a second distillation.

After enumerating the properties of this liquid or aqueous acid, Balard proceeds to show the mode of obtaining from it the pure gaseous acid: this he effected by throwing up into an inverted jar of mercury a quantity of the liquid acid, and then passing into it, through the mercury, small fragments of fused nitrate of lime, which abstracts the water and liberates the pure *hypochlorous acid* in the state of a gas, a little deeper colored than chlorine, of a strong penetrating odor, and absorbable by mercury, from the contact of which it is preserved in the above mode of obtaining it, by the layer of solution of nitrate of lime. Water dissolves many times its volume, forming a pale-colored solution, similar to that originally obtained by distillation in vacuo. A slight elevation of temperature is sufficient to decompose this gas with explosion and evolution of heat and light, so that it requires careful management. It is not changed by some hours' exposure to diffused daylight, but direct solar rays decompose it in a few minutes without explosion: when mixed with hydrogen and inflamed, it detonates violently, but at common temperatures the mixture remains unchanged. Bromine and iodine slowly decompose it; sulphur, selenium, phosphorus, and arsenic decompose it with sudden and violent detonation; charcoal also causes it to explode, apparently in consequence of the condensation which the gas suffers in its pores. Blotting-paper introduced into the gas also causes its sudden decomposition into a mixture of chlorine and oxygen; indigo decomposes it slowly and with more complicated changes; by the action of oxalic acid it forms carbonic acid, and chlorine is evolved.

Balard found, by various analytical methods, that the composition of this hypochlorous acid gas is analogous to that of Davy's euchlorine; that

is, that it consists of 1 volume of chlorine and 0.5 volume of oxygen, condensed into 1 volume; but he gives reasons (which we shall again advert to in speaking of some of the hypochlorites) for regarding the equivalent of the hypochlorous acid, not as $36 + 8 = 44$, but as $72 + 16 = 88$; that is, as Cl_2O_2 .

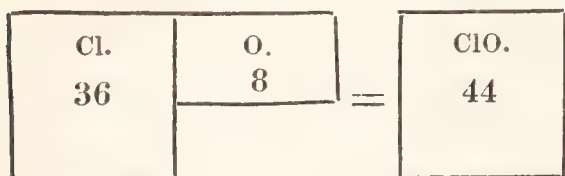
The concentrated aqueous solution of this acid is pale yellow; it has a peculiar penetrating odor, and an acrid but not acid taste; it attacks the cuticle with great energy, destroying it more rapidly than nitric acid, and communicating to it a reddish-brown color. It decomposes at common temperatures, and in summer requires to be kept in ice, and in a dark place. It is rapidly decomposed by iron-filings, but of the other heavy metals there are few which have any very energetic action upon it. It is curious that, with the exception of silver, they become oxidized and evolve chlorine; silver, on the contrary, evolves oxygen, and combines with the chlorine. It converts bromine and iodine into bromic and iodic acids; and sulphur, phosphorus, selenium, and arsenic, into their acids, with the evolution of chlorine. When a concentrated solution of this acid is mixed with ammonia, or when a fragment of sulphate or phosphate of ammonia is suspended in it, drops of the *explosive chloride of nitrogen* are formed: if both solutions are concentrated, effervescence and decomposition ensue.

Gay Lussac (*Ann. Ch. et Ph.*, 3 Ser., v. 273) has more lately added some important facts respecting this compound of chlorine and oxygen, which he terms *chlorous acid*, and gives reasons for regarding its equivalent as $36 + 8 = 44$, or its formula as ClO . He obtains it by filling a stopper bottle with dry chlorine and introducing into it a tube sealed at one end, two-thirds filled with peroxide of mercury, and the remaining third with fine dry sand (the use of which, however, is not very apparent). The stopper should be slightly greased in its upper part, so as to fit hermetically. The bottle is then inverted and shaken a little, by which the contents of the tube are brought into contact of the chlorine, the color of which soon *disappears*, and on opening the stopper under mercury a diminution of volume to about one-half is found to have taken place, and the remainder is gaseous chlorous acid*; it is *colorless*, and very unstable, exploding sometimes at common temperatures; it is very soluble in water, which takes up more than 100 times its volume; its aqueous solution gradually decomposes, especially in solar light, and is resolved into chlorine, oxygen, and chloric acid: the solution also contains a little hydrochloric acid due to the subsequent action of the chlorine on the water: at a boiling heat the solution decomposes as rapidly as if exposed to light, chloric acid is formed, and oxygen and chlorine evolved, the latter predominating. Gay Lussac shows that the neutralizing power of this acid is such that 1 equivalent of it may be represented by ClO , and that the neutral chlorite of potassa is $\text{KO} + \text{ClO}$, and not Cl_2O_2

* Pelouze obtains hypochlorous acid by passing pure and dry chlorine over binoxide of mercury prepared by precipitation, well dried, and placed in a cooled glass tube; chloride of mercury is formed, and the gaseous hypochlorous acid evolved and col-

lected by displacement. The crystalline oxide of mercury obtained by heat is scarcely acted on. When the gas is cooled to 0° , it condenses into a red liquid, explosive, and slowly soluble in water. (*Ann. Ch. et Ph.*, 3d Series, vii. 179.)

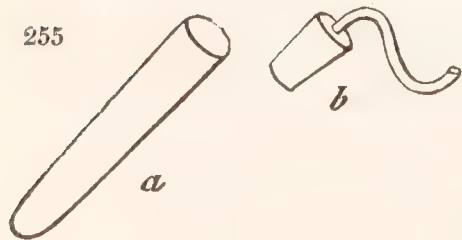
(as in the case of hyposulphurous acid, which is correctly represented by S_2O_2 , that being its equivalent in the neutral hyposulphites). In the formation of the gaseous acid, it would appear that 1 equivalent of oxide of mercury and 2 of chlorine produce 1 equivalent of chloride of mercury and 2 of chlorous acid, ($\text{HgO} + 2 \text{Cl} = \text{HgCl} + \text{ClO}$), and that in the latter,



1 volume of chlorine and half a volume of oxygen are condensed into 1 volume. Gay Lussac observes that the chlorous acid is probably weaker than the carbonic, though in most cases they mutually displace each other: the *chlorites*

are unstable compounds, decomposed by light and by a temperature of 212° into chlorates and chlorides: by the oxyacids they evolve chlorous acid. A chlorite mixed with a sufficiency of a metallic chloride and excess of sulphuric acid, effervesces, and the metal of the chloride takes the oxygen of the chlorous acid to become soluble in the sulphuric acid, whilst the chlorine of the chloride and of the acid are disengaged; but if the sulphuric acid be carefully added so as only just to decompose the chlorite, chlorous acid (and not chlorine) is given off. (In the former case $\text{KCl} + \text{KO}, \text{ClO} + 2 \text{SO}_3$ yield $2 [\text{KO}, \text{SO}_3]$ and 2Cl ; but in the latter, $\text{KCl} + \text{KO}, \text{ClO} + \text{SO}_3$ give $\text{KO}, \text{SO}_3 + \text{KCl} + \text{ClO}$.) In consequence of the feeble acid character of the chlorous acid and of the feeble basic character of oxide of mercury, no chlorate of mercury is formed when chlorine and oxide of mercury diffused in water are made to act on each other, but with the more powerful alkaline bases the case is different, and the chlorous acid, instead of remaining free, combines with them to form chlorites.

PEROXIDE OF CHLORINE. HYPOCHLORIC ACID. ClO_4 , was discovered by H. Davy, in 1815. (*Phil. Trans.*, p. 214.) He obtained it as follows: about 50 grains of chlorate of potassa are moistened with a few drops of concentrated sulphuric acid, and rubbed together with a platinum spatula, till they incorporate and form a solid mass of an orange color. This mass is to be introduced into a small glass retort, and gradually warmed in a water-bath, the temperature of which must be carefully kept below 212° , which may be managed by mixing alcohol with the water. (Or we may use a small tube, sealed at one end, as a substitute for a retort, and fitted with a cork perforated by



a small *S* tube, as in fig. 255, where *a* represents the tube, which should be wrapped round with a little tow, in case of explosion, to prevent fragments being thrown about; *b* the cork, &c.) A bright yellowish-green elastic fluid passes off, which is rapidly absorbed by water, but may be collected in small tubes over mercury.

Stadion obtained peroxide of chlorine by fusing into a mass one part of chlorate of potassa in a small glass retort, and when cold, pouring upon it three parts of oil of vitriol, and heating in a water bath. $3 [\text{KO}, \text{ClO}_5] + 4 \text{SO}_3 = 2 [\text{KO}, 2 \text{SO}_3] + \text{KO}, \text{ClO}_7 + 2 [\text{ClO}_4]$. In both these cases, but especially in the former, an explosion frequently ensues on mixing the acid with the chlorate, against which the operator should be on his guard.

The color of this gas is much deeper than that of chlorine, and to it the term *euchlorine* especially applies; its odor is peculiar, and unmixed with the smell of free chlorine. Its specific gravity compared with air, is, according to Davy, as 2·360 to 1·000; theoretically 2·338; compared with hydrogen it is as 34 to 1, 100 cubic inches therefore should weigh, at mean temperature and pressure, 72·012 grains. When peroxide of chlorine is heated to a temperature somewhat below that of boiling water, it explodes with much violence and the evolution of a bright light. The result of this decomposition is, that 2 volumes of the gas are expanded into 3, 2 of which are oxygen, and 1 chlorine; the relative weights, therefore, of its elements, are 32 of oxygen and 36 of chlorine. Two volumes detonated with 5 of hydrogen produce water and hydrochloric acid: $\text{ClO}_4 + 5 \text{H} = \text{HCl} + 4 \text{HO}^*$.

Its saturated aqueous solution (containing about 7 volumes of the gas to 1 of water) is of a deep yellow color, an astringent and corroding taste, and when applied to the tongue, leaves for a long time a very disagreeable sensation. It destroys vegetable colors. It is absorbed according to Martens (*Ann. Ch. et Ph.*, Lxi. 293,) by alkaline solutions, forming with them a peculiar class of bleaching salts.

Faraday condensed this gas by inclosing the mixture of chlorate of potassa and sulphuric acid in a sealed tube, and leaving them to act upon each other for twenty-four hours. In that time there had been much action; the mixture was of a dark reddish-brown, and the atmosphere within of a bright yellow color. The mixture was then heated up to 100° , and the unoccupied end of the tube cooled to 0° : by degrees, the mixture lost its dark color, and an ethereal-looking liquid condensed. It was not miscible with a small portion of the sulphuric acid which lay beneath it; but when returned on to the mass of salt and acid, it was gradually absorbed, rendering the mixture of a much deeper color. "The peroxide of chlorine thus obtained is a very fluid transparent substance of a deep yellow color. A tube containing a portion of it in the clean end was opened at the opposite extremity; there was a rush of euchlorine vapor, but the salt plugged up the aperture: whilst clearing this away, the whole tube burst with a violent explosion." (*Phil. Trans.*, 1823, p. 194.) This liquid peroxide of chlorine was solidified by exposure to the cold of the solid carbonic acid and ether bath: in this state it resembled in appearance bichromate of potassa: it was moderately hard, brilliant, and transparent: it melted at 75° below 0° , and the solid portion was heavier than the liquid. In the solid state it gave off so little

* For the purpose of illustration, in lectures, this gas may be conveniently obtained by putting a few grains of chlorate of potassa into the bottom of a tall narrow tube or jar (half an inch diameter and about twelve high), standing upon a foot, and carefully dropping in upon the salt, so as not to soil the sides of the tube, a little sulphuric acid: the peroxide of chlorine is immediately evolved (provided no explosion ensues), and its weight causes it to expel the superincumbent air and fill the tube, from which, with a little management, it

may be decanted through the air, into a tall glass containing copper-leaf, upon which it exerts no action; but a hot wire dipped into the gas, causes it immediately to explode, and the metal then burns in the mixed oxygen and chlorine. A little jet of nitric oxide thrown in, produces the same effect, without explosion. The first action of the sulphuric acid upon the salt is much less apt to cause explosion when it has been previously fused and broken into small fragments, than when in its usual crystals.

vapor that the air over it was not discolored, so that the pressure of its vapor at that temperature must be very small. "Some hours afterwards, wishing to solidify the same portion of euchlorine which was then in a liquid state, I placed the tube in a bath at -110° , but could not succeed either by continuance of the tube in the bath, or opening the tube to allow the full pressure of the atmosphere; but when the liquid euchlorine was touched by a platinum wire, it instantly became solid. There are many similar instances among ordinary substances, but the effect in this case makes me hesitate in concluding that all the gases which as yet have refused to solidify at temperatures as low as 166° below 0° , cannot acquire the solid state at such a temperature." (FARADAY, *Phil. Trans.*, 1845, p. 167.)

Sir H. Davy found that, of the unmetallic combustible substances, phosphorus was the only one which spontaneously decomposed this gas: the phenomena were the same as with the protoxide of chlorine. He analysed it by detonation with hydrogen as above described. He says that when it is absorbed by solution of potassa, chlorate of potassa and chloride of potassium are the results. According to Davy and Gay Lussac, this gas consists of

						Volumes.	S. G.
Chlorine	1	...	36	...	52.9	0.5	1.23
Oxygen.....	4	...	32	...	47.1	1	1.10
<hr/>							
Peroxide of chlorine	1		68		100.0	1	2.33

CHLORIC ACID. ClO_5 . This acid was discovered by Gay Lussac (*Ann. de Chim.*, xci. 108). It cannot exist independent of an atom of water, or of some base, so that it has not been obtained *anhydrous*; the hydrated acid in its state of extreme concentration, being $\text{HO} + \text{ClO}_5$, or $\text{H} + \text{ClO}_6$.

Hydrated chloric acid may be prepared, (1.) by passing a current of chlorine through a mixture of oxide of silver and water. Chloride of silver is produced, which is insoluble, and may be separated by filtration: the excess of chlorine, which the filtered liquor contains, is separable by heat, and the chloric acid dissolved in water remains. (2.) By adding dilute sulphuric acid to a solution of *chlorate of baryta*, as long as it occasions a precipitate. The baryta is thus separated in the form of an insoluble sulphate, and the chloric acid remains in aqueous solution. Care must be taken to add no more sulphuric acid than is requisite; for any excess contaminates the chloric acid. If the exact proportion has been used, the chloric acid is neither rendered turbid by dilute sulphuric acid nor by chlorate of baryta. If either of these occasion a precipitate, they must be *carefully* added till the effect ceases; the clear liquid may then be decanted or filtered off. It may be concentrated by cautious evaporation. (GAY LUSSAC.) (3.) By exposing an aqueous solution of oxide of chlorine to the sun's rays till colorless, and expelling the chlorine by a gentle heat. (L. GMELIN.) (4.) By the action of fluosilicic acid on chlorate of potassa. A hot aqueous solution of chlorate of potassa is mixed with excess of fluosilicic acid; the sour liquid, when cold, is filtered, evaporated below 80° , and, after two days, filtered through powdered glass. (I. L. WHEELER. SERULLAS.)

Hydrated chloric acid is a sour liquid, and of a yellowish tint when

highly concentrated. It forms no precipitate in any metallic solution. It reddens vegetable blues, and then bleaches them. When added to a strong solution of potassa, crystals of chlorate of potassa are deposited. When concentrated, it acts powerfully, and even to ignition, upon paper, and some other dry organic bodies; it decomposes alcohol, with the formation of acetic acid. The most remarkable of its salts, which are now termed *chlorates*, were formerly known under the name of *oxymuriates*, or *hyperoxymuriates*. When distilled at a higher heat than 100° , it suffers decomposition, and a portion of chlorine and oxygen are liberated, perchloric acid passing over, but no chloric acid. It is decomposed by hydrochloric acid into chlorine and water; $5\text{HCl} + \text{ClO}_5 = 5\text{HO} + 6\text{Cl}$: by excess of sulphurous acid into sulphuric, and hydrochloric acids; $6\text{SO}_2 + \text{ClO}_5, \text{HO} = 6\text{SO}_3 + \text{HCl}$: and by excess of sulphuretted hydrogen into water, hydrochloric acid, and sulphur; $6\text{HS} + \text{ClO}_5 = 5\text{HO} + \text{HCl} + 6\text{S}$. Those acids which are already saturated with oxygen do not act upon it. Chloric acid consists of

Chenevix. Gay Lussac. Volumes.									
Chlorine	1	...	36	...	47.4	...	45	...	46.8
Oxygen	5	...	40	...	52.6	...	55	...	53.2
<hr/>									
Chloric acid .	1		76		100.0		100		100.0

Chlorates. These salts are either $\text{MO} + \text{ClO}_5$ or $\text{M} + \text{ClO}_6$. They deflagrate powerfully with combustible matter, and often by mere friction. (See *Chlorate of Potassa*.) They are all soluble in water. By heat they are mostly resolved into chlorides and evolve oxygen.

PERCHLORIC, OXYCHLORIC, OR HYPERCHLORIC ACID, ClO_7 , or as hydrate $= \text{HO}, \text{ClO}_7$, or H, ClO_8 , was discovered by Count Stadion (*Ann. de Ch. et Ph.*, viii.): it is procured in its state of hydrate, (1.) by distilling *perchlorate of potassa* with its own weight of sulphuric acid, diluted with about a fourth part of water. At a temperature of about 280° , white vapors pass off, which condense in the form of a colorless liquid. (2.) By boiling perchlorate of potassa with excess of fluosilicic acid; on cooling the duly evaporated mixture, glutinous silicofluoride of potassium falls, which must be separated by filtering; evaporate, cool, filter again, evaporate further, and lastly distil. (SERULLAS.) (3.) By the mutual decomposition of atomic equivalents of perchlorate of baryta and sulphuric acid. (O. HENRY.) It is a very stable compound, not decomposed by sulphuric or hydrochloric acid; nor by alcohol or organic bodies. When concentrated, its specific gravity is 1.6, and it boils at 392° . By distillation with strong sulphuric acid it may be obtained in the solid form and crystallized; in this state it hisses when thrown into water. (GAY LUSSAC. SERULLAS. MITSCHERLICH. *Ann. Ch. et Ph.*, viii., ix., XLvi., and XLix. See also NATIVELLE on the preparation of this acid. *Journ. der Pharm.*, and *Ch. Gaz.*, May, 1843.) Anhydrous perchloric acid has not been isolated: it consists of

Volumes.							
Chlorine	1	...	36	...	39.1	...	1.0
Oxygen	7	...	56	...	60.9	...	3.5
<hr/>							
Perchloric acid .	1		92		100.0		

Perchlorates. Oxychlorates. These salts have the formula $\text{MO} + \text{ClO}_7$, or $\text{M} + \text{ClO}_8$. Although more abundant in oxygen, they are

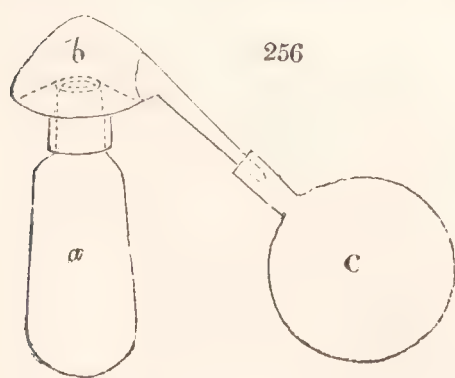
of less explosive tendency, and less easily decomposed by heat than the chlorates, like which they are resolved either into chlorides and oxygen gas, or into oxides, oxygen, and chlorine: they are all soluble in water.

§ III. IODINE. I. 126.

IODINE was discovered in 1812 by M. Courtois, a chemical manufacturer at Paris. Vauquelin (*Ann. de Ch.*, xc.), Gay Lussac, in 1813, (*Ibid.* LXXXVIII., xc., and xci.), and Davy (*Phil. Trans.*, 1814), have fully examined its properties.

Iodine is chiefly prepared at Glasgow from *kelp*, which is the fused ash obtained by burning sea-weeds, and is principally manufactured on the west coast of Ireland, and the western islands of Scotland. The long stems of the *Fucus palmatus* are most productive of iodine. "A high temperature in the preparation of kelp, which increases the proportion of alkaline carbonate, diminishes that of the iodine, owing to the volatility of the iodide of sodium at a full red heat. The kelp which contains most iodine generally also contains most chloride of potassium, and it is for these two products that the substance is now valued, more than for its alkali." (GRAHAM.) Traces of iodine have also been discovered in several plants growing near the sea. (*Ch. Gaz.*, Jan. 1843.) Traces of it are also found in sea water, in sponge, in several saline springs, and in the coarser varieties of common salt; Vauquelin detected it in some silver ores from Mexico (*Ann. Ch. et Ph.*, xxix.); and Bustamente, in a white lead ore from Mexico, and in a species of *Agave*. (*Ann. Ch. et Ph.*, LXXII.) It has also been detected in cod liver oil, and in the oil of the liver of the skate (*Ch. Gaz.*, Mar. and Apr., 1843); in the *Nasturtium aquaticum*, by Muller (*Ann. der Pharm.*, July, 1843,) and in the yellow sap of the *Iulus fetidissimus*, by Holl. (See L. GMELIN, *Handbuch*, for a detailed enumeration of the sources of iodine.)

Iodine may be procured by the following process: Lixivate powdered kelp with cold water. Evaporate the lixivium till a pellicle forms, and set aside to crystallize. Evaporate the mother-liquor to dryness, and pour upon the mass half its weight of sulphuric acid. Apply a



gentle heat to this mixture in the flask *a* of the alembic shown in the annexed figure, of which *b* is the head or capital, having a tube issuing from it, and descending into the receiver *c*. Fumes of a violet color arise, (hence its name, from *ἰώδης*, *violaceus*,) and condense in the form of opaque crystals, having a metallic lustre; these are to be washed out of the head of the alembic with

a small quantity of water, and quickly dried on bibulous paper.

Iodine may likewise be obtained from soap-makers' *black ash* by a similar process: instead of evaporating the mother-liquor to dryness, the quantity of iodine is sometimes greater when it is merely concentrated, mixed with excess of sulphuric acid, boiled, and filtered; the liquid is then mixed with its weight of powdered black oxide of manganese, and heated in an alembic, or in a flask with a wide tube attached to its neck, when the iodine sublimes as before.

According to Dr. Ure, iodine may be abundantly obtained from the brown residuary kelp-liquor of the soap-boilers, by exposing it to a heat of about 230° , saturating it with sulphuric acid previously diluted with its bulk of water, and pouring the liquor, when cold, off the crystals which are deposited, and which are chiefly sulphate of soda. Filter this liquor, and to every 12 ounces by measure add 1000 grains of black oxide of manganese in powder; put this mixture into a large matrass with a wide neck, over which a glass globe is inverted, and apply heat with a charcoal chauffer. The less diffusive heat of a lamp is apt to crack the bottom of the matrass, particularly if a large quantity of materials be employed. To prevent the heat from acting on the globular receiver, a thin disc of wood, having a round hole in its centre, is placed over the shoulder of the matrass. As soon as the upper vessel becomes warm, another is to be put in its place, and thus the two may be used in rotation as long as violet fumes arise. The process as conducted at Glasgow is described by Professor Graham in his *Elements of Chemistry*. Some useful directions respecting it are also given in the *Philosophical Magazine*, LX.

To obtain perfectly pure iodine, Millon recommends passing chlorine through a solution of pure iodide of potassium, till the evolved iodine is redissolved, and then pouring the solution into another solution of iodide of potassium containing at least three times as much of the iodide: the iodine is precipitated, and only requires to be washed and dried.

The iodine of commerce may be sufficiently purified by solution in alcohol, filtering, and precipitating it by the addition of water.

Iodine has a grey or bluish-black color; its lustre is metallic, and its fracture when in a mass is greasy and lamellar. It is a non-conductor of electricity. (Fused iodine conducts the current of 60 to 90 pairs of plates. KNOX, *Ph. Mag.*, xvi. 188.) It is not changed by passing through a red-hot tube, either alone or over charcoal. It is soft and friable. Its specific gravity, according to Gay Lussac, is 4.946. Its specific heat = 0.05412. (REGNAULT.) It produces a yellow stain upon the skin. Its smell somewhat resembles that of diluted chlorine; its taste is acrid. It is extremely volatile when moist, and in that state produces a pale violet vapor at a temperature of between 60° and 80° . At 120° or 130° it rises more rapidly in vapor; at 220° it fuses; and at 350° it boils and produces dense violet-colored fumes, which condense in brilliant plates, and acute octoëdrons. 100 cubical inches of iodine vapor weigh 270.8036 grains. Its specific gravity, therefore, compared with air, is 8.7356, and with hydrogen, 126. The experimental density of iodine vapor is 8.716. (DUMAS.) Like chlorine and oxygen, it is evolved from its combinations at the positive electrode; it renders vegetable colors yellow, and is very sparingly soluble in water, that liquid not holding more than one 7000th its weight in solution. (Jacquelain, in his essay on starch, (*Ann. Ch. et Ph.*, LXXIII.) attributes greater solubility to iodine.) The color of this solution is pale brown; it gives out no oxygen by exposure to sunshine, nor does it bleach; it, however, slowly loses its own color, and gives rise to the formation of *iodic* and of *hydriodic acid*. Iodine is much more soluble in alcohol and in ether, forming deep brown solutions.

The peculiar appearance of the vapor of iodine is in many cases a sufficient evidence of its presence; a more delicate test, however, was

discovered by Colin and Gaultier de Claubry, in its remarkable property of forming a deep blue compound with starch. According to Stromeyer, a liquid, containing one 450,000th its weight of iodine, receives a blue tinge when a solution of starch is added to it. To ensure success, the iodine must be in a free state, and the solution cold, for boiling water destroys the color; where the proportion of iodine is very minute, a few minutes elapse before the discoloration ensues. (STROMEYER, *Gilbert's Annalen*, xix. 146.) As the iodic compounds are decomposed by chlorine, it may often be conveniently used as a test of iodine. Thus, when a very minute quantity of iodide of sodium or potassium is present in a solution, the addition of chlorine discolors it, and if a little solution of starch be then added, the iodine is detected by the blue color. Or any compound containing common salt and an alkaline iodide, mixed with a solution of starch, and exposed to voltaic action, yields a blue color at the positive electrode. The equivalent of iodine may be assumed as = 126 (126.3, TURNER; 126.57, GRAHAM; 125, GAY LUSSAC.)

The principal use as yet made of iodine and its compounds, is in medicine; it powerfully promotes the action of the absorbents, and is chiefly used in glandular diseases, and as an alterative. In over-doses it is an irritant poison. The rich color of some of its metallic combinations has also led to its employment in the art of calico-printing.

Iodine is occasionally adulterated by plumbago, sulphuret of antimony, or peroxide of manganese, but these additions are easily detected by their insolubility in alcohol. The relative quantity of moisture in iodine may be ascertained by heating it in a tube, with twice its weight of fused chloride of calcium, at a temperature not exceeding the boiling-point of the iodine; the iodine may be expelled by a current of air, and the increase of weight sustained by the chloride gives the quantity of water.

IODINE AND OXYGEN. There appear to be four definite compounds of iodine with oxygen; namely, an oxide, and three acids; but of these, the iodic and periodic acids only have been duly examined.

OXIDE OF IODINE was discovered by Sementini, in attempting the direct combination of iodine and oxygen: a portion of it, he says, is formed when iodine is repeatedly heated in atmospheric air, but it is most rapidly produced by presenting iodine and oxygen to each other at a high temperature. For this purpose, a bladder of oxygen is affixed to one end of a copper tube, so placed as to be heated red-hot by lamps or a small charcoal fire; the other end of the tube terminates in the bulb of a tubulated retort containing iodine, which is also to be heated by a lamp: the oxygen is then propelled through the hot tube into the vapor and upon the hot iodine, and a yellow and very thick oleaginous liquid distils over, of an acrid disgusting taste and odor, which is the compound in question. It slowly volatilizes in the air, and is very soluble in water and alcohol, producing amber-colored solutions. Phosphorus and potassium are inflamed by it. It changes the blue of litmus to green. If an alkali be poured into its solution, it is rendered colorless. Its composition is not correctly known.

IODOUS ACID. If excess of oxygen, and a considerable degree of heat, be employed in the preceding experiment, the product is partly *iodous acid*. This acid is best obtained by introducing a mixture of one part of

iodine and three of chlorate of potassa into a retort, and rapidly applying heat: a dense fluid distils over, which should be collected in a receiver cooled by a freezing-mixture. It has a pungent taste and peculiarly disagreeable odor: its specific gravity exceeds that of water. It reddens litmus, and forms a yellow solution when diluted with water; it slowly evaporates when exposed to air, and rapidly volatilizes at 112° . It is decomposed by sulphur, disengaging a little heat, and liberating violet vapors; sulphurous acid also decomposes it. Phosphorus and potassium are instantly inflamed by it. It is without action on carbon. It dissolves iodine. Neither its composition, nor that of the oxide, have been accurately determined. (*Quarterly Journal*, xvii. 381: *Ibid. New Series*, i. 477.) It appears probable, from the experiments of Wöhler, that the compound obtained when chlorate of potassa is used, contains chlorine. By the spontaneous evaporation of a solution of iodine in a dilute solution of soda, Mitscherlich obtained prismatic crystals, which by the action of hot water were converted into iodate of soda and iodide of sodium: he considers them as an *iodite* of soda. (*Ann. Ch. et Ph.*, xxxvii. 84.) According to Millon (*Ann. Ch. et Ph.*, November, 1844,) a yellow compound = IO_4 , which he calls *hypoiodic acid*, is one of the results of the action of nitric acid on iodine: it is also obtained by the action of sulphuric on iodic acid.

IODIC ACID. IO_5 . (DAVY, *Phil. Trans.*, 1815.) This compound cannot be obtained by the direct action of oxygen on iodine: it is formed, (1) by acting upon peroxide of chlorine by iodine: for this purpose the iodine may be introduced into a small flask, and the peroxide of chlorine disengaged upon it from a proper mixture of chlorate of potassa and sulphuric acid, with the precautions above pointed out: or 100 grains of chlorate of potassa may be introduced into a small retort, with 400 grains of hydrochloric acid, of the specific gravity 1.105: annex to the retort a small globular receiver, having a bent tube issuing from it, and passing to the bottom of a small flask containing about 50 grains of iodine; carefully apply the heat of a lamp to the retort, by which oxide of chlorine will be disengaged, which will be decomposed and absorbed by the iodine. A compound is thus formed, which consists of chloride of iodine and iodic acid. The former is separable by a gentle heat; the latter remains as a white, deliquescent, semitransparent, sour, and inodorous body, very soluble in water, and of a specific gravity exceeding 2. (2) Iodic acid may also be precipitated by slowly adding excess of ether, or of alcohol, to the strong aqueous solution of the perchloride of iodine. (3) This acid is also formed by boiling iodine for several hours with about five times its weight of strong nitric acid. The mixture should be introduced into a tube closed at one end, and the iodine, as it sublimes to the upper part, constantly returned into the acid, till it disappear: on carefully driving off the nitric acid by heat, the iodic acid remains. (CONNELL.) (4) Iodic acid is also obtained by the decomposition of *iodate of soda* (which see) by sulphuric acid, (SERULLAS, *Ann. Ch. et Ph.*, xliii. 216); (5) and by the decomposition of iodate of baryta by dilute sulphuric acid (see *Iodate of Baryta*). (6) Millon gives the following as the best process for preparing iodic acid (*Ann. Ch. et Ph.*, Decr., 1843):—80 parts of pure iodine, 75 of chlorate of potassa, 1 of nitric acid, and 400 of water are mixed in a

glass balloon or flask of sufficient capacity, and raised to the boiling point, the heat being removed as soon as chlorine begins to be abundantly disengaged. When the iodine has disappeared, 90 parts of nitrate of baryta (or its equivalent of chloride of barium) are dissolved in water, and added to the mixture in the flask: the precipitated iodate of baryta is then washed two or three times by decantation, and boiled for half an hour with 40 parts of sulphuric acid diluted with 150 of water; the liquor is then filtered off and evaporated, when crystals of iodic acid are obtained on cooling: to render these perfectly pure, they must be re-dissolved and boiled with a little iodate of baryta; the solution filtered, evaporated to dryness, and the dry iodic acid heated so as to expel any traces of nitric (or hydrochloric) acid; it may then be re-dissolved and crystallized, but the crystals now are smaller and less distinct than when formed in water acidulated by a mineral acid.

The aqueous solution of iodic acid first reddens and then destroys vegetable colors; concentrated by evaporation, it affords a pasty mass, which is *hydrated iodic acid*, IO_5, HO , and which may be crystallised in hexagonal laminæ, from which the water may be driven off by the careful application of a higher temperature; at about 500° it fuses, and is decomposed into oxygen and iodine. There is also, according to Millon, a hydrate $= 3 \text{IO}_5, \text{HO}$, which is nearly insoluble in alcohol, whereas the anhydrous and the common hydrated acid are soluble in about two parts of alcohol. Iodic acid acts powerfully upon the metals, and with the oxides forms a class of salts called *iodates*. Nitric, sulphuric, phosphoric, and boracic acids, when dropped into a hot saturated solution of iodic acid, form crystals of a yellowish color, composed of the two acids. Iodic acid is decomposed by hydrochloric and by oxalic acid. When it is mixed with charcoal, sulphur, and some other combustibles, it forms compounds which deflagrate when heated: its compounds also deflagrate, like the chlorates, when thrown upon red-hot charcoal. The solution of iodic acid is decomposed by several organic substances, as by morphia, narcotin, and pyrogallie acid; and by saliva, in consequence of the sulphocyanide there present. Iodic acid is composed, according to Gay Lussac, of

Iodine.....	1	126	75.9
Oxygen	5	40	24.1
<hr/>					
Iodic acid	1	166	100.

IODATES. These salts are represented by the general formula $\text{MO} + \text{IO}_5$, or $\text{M} + \text{IO}_6$. By heat they either become iodides, losing 6 atoms of oxygen, or they lose iodine and 5 atoms of oxygen, leaving a metallic oxide. Their deflagration with combustibles is less powerful than that of the chlorates: they are mostly difficultly soluble. (C. RAMMELSBERG. *Poggend.* xliv. 525. MILLON; *Ann. Ch. et Ph.* ix. 407.)

OXIODIC ACID. PERIODIC ACID. IO_7 . (1) When a solution of iodate of soda, mixed with pure soda, is saturated by chlorine, and concentrated by evaporation, a sparingly soluble white salt is obtained, which is a *periodate of soda*: when it is dissolved in dilute nitric acid, and mixed with nitrate of silver, a yellow precipitate falls, which, dissolved in hot nitric acid and evaporated, yields orange-colored crystals of *periodate of*

silver. These crystals are decomposed by cold water, a yellow insoluble *subperiodate* of silver falls, and an aqueous solution of pure periodic acid is formed, which yields crystals of the *hydrated periodic acid*, $\text{HO} + \text{IO}_7$, or $\text{H} + \text{IO}_8$, by evaporation, and which, at a temperature above 212° , are resolved into oxygen and iodic acid. (2) Periodate of soda is dissolved in the smallest possible quantity of warm dilute nitric acid and a solution of nitrate of lead added, so as to precipitate periodate of lead, which may be decomposed by digestion with sulphuric acid not added in excess: the resulting solution of periodic acid should be decanted off the insoluble residue, and evaporated so as to yield crystals. (BENCKISER. *Ann. Pharm.* xvii. 214: AMMERMÜLLER and MAGNUS: *Poggend.* xxviii. 514.) The periodic acid consists of

Iodine	1	126	69
Oxygen	7	56	31
<hr/>					
Periodic acid	1	182	100

PERIODATES. The salts of the periodic acid are represented by the formula $\text{MO} + \text{IO}_7$ or $\text{M} + \text{IO}_8$; at a red heat they are decomposed with the same phenomena as the iodates: they are mostly of difficult solubility.

IODINE AND CHLORINE. PROTOCHLORIDE OF IODINE. ICl . When chlorine is conducted into a vessel containing iodine, it is quickly absorbed, and a compound obtained, which is brown when the iodine is in excess, colorless when exactly saturated, and yellow if there be excess of chlorine. Of these compounds the first appears to be a protochloride: it is a red-brown liquid, having the mixed odor of chlorine and iodine, irritating the eyes, and sour, astringent, and pungent to taste; it is hygrometric, tinges the cuticle dark yellow, bleaches indigo and litmus, and does not blue starch. When gently heated, perchloride is evolved, and iodine remains: aqueous sulphurous acid and sulphuretted hydrogen separate iodine. With solutions of potassa and soda it yields chlorides, iodates, and free iodine, which excess of the alkali converts into iodide and iodate. $6 \text{KO} + 5 \text{ICl} = 5 \text{KCl} + \text{KO}, \text{IO}_5 + 4 \text{I}$. With ammonia sal ammoniac is formed, and iodide of nitrogen precipitated. $3 \text{ICl} + 4 \text{NH}_3 = 3 [\text{NH}_4, \text{Cl}] + \text{NI}_3$. The aqueous solution of protiodide of chlorine is obtained by passing a small quantity of chlorine into water holding excess of iodine; when shaken with ether the chloride is abstracted, and may be obtained by the evaporation of the ether. According to the experiments of Kane (*Phil. Mag.*, x. 430,) this chloride consists of

					Kane.
Iodine	1	126	77.7
Chlorine	1	36	22.3
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Protochloride of Iodine .	1	162	100.0

PERCHLORIDE OF IODINE, ICl_3 , is obtained by passing dry chlorine in great excess over dry iodine gently heated; it is yellow, and after fusion forms acicular crystals. In its action upon other bodies it closely resembles the protochloride. It fuses between 70° and 80° , evolving chlorine, which it again absorbs on cooling. Ether does not abstract it from its aqueous solution. With solution of potassa perchloride of iodine

yields chloride and iodate, and iodine is separated, provided there be not excess of alkali. $5 \text{ICl}_3 + 18 \text{KO} = 15 \text{KCl} + 3 [\text{KO}, \text{IO}_5] + 2 \text{I}$. (LIEBIG.) Perchloride of iodine is thrown down from its aqueous solution by sulphuric acid, which if added gradually in a cooled vessel, yields first a white caseous and then yellow precipitate, soluble on heating the mixture, but again separating on cooling.

						Kane.
Iodine	1	126	53·84 54·34
Chlorine	3	108	46·16 45·66
<hr/>						
Perchloride of Iodine.....	1	234	100·00 100·00

§ IV. BROMINE. Br. 78.

BROMINE was discovered in 1826 by M. Balard, of Montpellier. It was originally obtained from the uncrystallizable residue of sea-water commonly called *bittern*: a current of chlorine passed through this liquid gives it an orange tint, in consequence of the evolution of bromine from its combinations: a portion of sulphuric ether is then shaken up with it, which, as it separates upon the surface, is found to have abstracted the bromine, and acquired a reddish-brown tint. The ethereal solution is agitated with a strong solution of potassa, by which a solution of bromate of potassa and bromide of potassium is formed: the ether, floating upon the surface, may be separated and used again; the denser liquid is then evaporated to dryness, and the residue exposed to a dull-red heat leaves *bromide of potassium*. This is mixed with half its weight of binoxide of manganese, and its weight of sulphuric acid previously diluted with half its weight of water, and the mixture distilled into a cold receiver containing water, and into which the beak of the retort or condenser dips. The deep orange-colored vapor of bromine condenses, and the liquid bromine, separated from the water, is afterwards dehydrated, if necessary, by distilling it off chloride of calcium. Should the fluid from which the bromine is to be obtained contain iodine, it must be separated in the form of iodide of copper by the addition of a solution of sulphate of copper. (BALARD.)

Bromine probably exists in sea-water in the state of bromide of magnesium, but its relative proportion is exceedingly minute. One hundred pounds of sea-water, at Trieste, afforded only 5 grains of bromide of sodium = 3·3 grains of bromine: it is there unaccompanied by iodine; and the same is the case, according to Hermbstadt, in the waters of the Dead Sea. In the Mediterranean, on the contrary, iodine accompanies it.

The presence of bromine is recognized by evaporating the water, so as to separate its more ordinary crystallizable contents, reducing the remainder to a small bulk, and dropping in a concentrated solution of chlorine: in the absence of iodine, which may be detected by starch, the appearance of a yellow tint announces bromine. It has thus been discovered in certain salt springs, in the ashes of marine plants, and in those of some marine animals. Among the saline springs most abundant in bromine are those of Theodorshal, near Kreutznach in Germany; these are now the chief source of bromine as an article of commerce.

At common temperatures and pressures bromine is a deep reddish-

brown liquid, of a strong disagreeable odor, something resembling that of oxide of chlorine, whence its name (from *βρωμος*, *graveolentia*); its specific gravity is about 3 (2.96 to 2.99). It emits a brownish-red vapor at common temperatures, and it is said that when this vapor is diffused through air, it is upon the whole less annoying than chlorine. It boils at 116° . At a temperature somewhat below 0° it congeals into a brittle solid. It is a non-conductor of electricity, and appears in the Voltaic circuit at the positive electrode. It suffers no change by transmission through red-hot tubes. It dissolves sparingly in water (1 part in 23, Löwig), forming a brown solution of an austere, but not sour taste, from which the bromine escapes by exposure, and rapidly by boiling: when long kept, especially if exposed to light, it becomes sour from the formation of hydrobromic acid. It forms, under certain circumstances, a definite *hydrate*, which, according to Löwig (*Poggendorf's Annalen*, xiv. 114) is obtained by exposing bromine with a small quantity of water to a temperature of 32° ; red octohedral crystals of the *hydrate of bromine* are then deposited, which continue permanent at the temperature of 50° , and contain 10 equivalents of water. At a higher temperature they decompose into liquid bromine and aqueous solution of it. The hydrate is also obtained by passing the vapor of bromine through a moistened tube cooled nearly to the freezing-point. Bromine dissolves in alcohol, and more abundantly in ether. It destroys vegetable colors. It communicates an orange tint to solution of starch. When a burning taper is immersed into its vapor it is speedily extinguished, the flame previously assuming a green and red tint. Phosphorus spontaneously inflames in its vapor; tin and antimony also burn in it; it combines with potassium with explosive violence. Its action on alkaline solutions is analogous to that of chlorine and iodine. It stains the skin of a yellow color; acts with energy upon most vegetable and animal substances, and is fatal to animal life; a single drop placed upon the beak of a bird immediately kills it. The specific gravity of bromine vapor has not been correctly determined, but its equivalent number appears, from Berzelius' analysis of bromide of silver, to be about 78, which ought also to express the specific gravity of its vapor compared with hydrogen. The density of this vapor compared with air will, therefore, be about 5.4, and 100 cubical inches will weigh about 167 grains. According to Dr. Thomson, the density of bromine vapor theoretically deduced is 5.555. The alcoholic solution of bromine, and the bromide of sodium, are occasionally used in medicine: and from its powerful action, there can be no doubt that it must contribute to the medicinal powers of the mineral waters in which it exists.

BROMOUS ACID. BrO . The existence of this compound has been rendered probable by the experiments of Gay Lussac (*Ann. Ch. et Ph.*, v. 304, 3 Ser.), who states that he obtained a gaseous bromous acid by a process similar to that by which he obtained chlorous acid.

BROMIC ACID. BrO_5 . Bromic acid is obtained by the decomposition of a solution of *bromate of baryta* by sulphuric acid: sulphate of baryta is precipitated, and a solution of bromic acid obtained, which may be concentrated by slow evaporation; at a high temperature it is partly decomposed, and cannot be obtained anhydrous. It is colorless, sour, inodorous, and first reddens, and then destroys the blue of litmus. It is

partially decomposed by concentrated sulphuric acid, but not by nitric acid. It is decomposed by sulphurous acid, by sulphuretted hydrogen, and by hydriodic and hydrochloric acids. From the analysis of bromate of potassa there can be no doubt that the bromic acid is analogous in composition to the chloric and iodic acids, and that it consists of

						Balard.
Bromine	1	78	66.1 64.69
Oxygen	5	40	33.9 35.31
<hr/>						
Bromic acid	1	118		100.0	100.00

BROMATES. These salts are represented by $\text{MO} + \text{BrO}_5$, or $\text{M} + \text{BrO}_6$: they are resolved at a red heat either into bromides and 6 atoms of oxygen, or into 5 atoms of oxygen and 1 of bromine, a metallic oxide being left: they deflagrate with combustibles like the chlorates. The formation of *perbromic acid*, BrO_7 , has not been accomplished.

CHLORIDE OF BROMINE. By passing chlorine through bromine, and condensing the resulting vapors at a low temperature, a reddish-yellow fluid is obtained, having a penetrating odor and disagreeable taste. It is very fluid and volatile, emitting yellow vapor; it dissolves in water, and the solution destroys vegetable colors: it would appear, therefore, not to decompose water. When this aqueous solution is cooled, crystals of hydrated chloride are deposited; and when exposed to sunshine, it yields hydrochloric and bromic acids. (LÖWIG.) Chlorine, as already stated, decomposes most of the compounds of bromine, and hence is useful as a test of its presence. When, for instance, aqueous chlorine is dropped into a weak solution of bromide of potassium, or of sodium, the evolution of bromine is manifested by the deep yellow color that is produced, and by the odor of the vapor of bromine.

IODIDE OF BROMINE. Iodine and bromine probably combine in two proportions, but the compounds have not been analyzed. In certain proportions (probably one atom of iodine and one of bromine) a solid body is obtained, which yields reddish-brown vapors when heated, and these readily condense into arborescent crystals. A further addition of bromine dissolves these, forming a dark-colored liquid, soluble in water, possessed of bleaching qualities, and yielding bromides and iodides with the alkalis.

Chlorine, iodine, and bromine, are occasionally so associated as to require separation in analyses. To ascertain the quantity of iodine in the mixed chlorides and iodides of mineral waters, Rose recommends precipitation by nitrate of silver; the mixed chloride and iodide of silver thus thrown down is fused, weighed, and afterwards heated in a tube and a stream of chlorine passed over it; the iodine is thus expelled, and the whole converted into chloride of silver; this is weighed again, and a loss is found to have taken place in consequence of the equivalent of the expelled iodine being greater than that of the expelling chlorine; this loss, multiplied by 1.389, gives the quantity of iodine originally present, and which has been replaced by the chlorine. Schweitzer recommends the adoption of a similar method for estimating the quantity of iodine when mixed with bromine; in this case the mixed iodide and bromide of silver is to be heated in an atmosphere of bromine vapor, by which the iodine is expelled. But the accurate determination of the relative quan-

tities of chlorine, bromine, and iodine, in cases where their combinations are blended, is a problem of much difficulty.

§ V. FLUORINE. F. 19.

THIS substance has not hitherto been isolated, for its powers of combination are such, that nobody has been found capable of resisting its action. The evidence of its existence as a distinct electro-negative element, will be more clearly understood by reference to the account of its compound with hydrogen (see *Hydrofluoric Acid*), and to the experiments of Sir H. Davy (*Phil. Trans.*, 1813, p. 263, and 1814). Its equivalent number is probably about 19 (18·75, BERZELIUS). It is found as a component of a few mineral substances only; one of these, however, commonly called *fluor-spar*, is very abundant; it is a compound of fluorine and calcium, or a *fluoride of calcium*. Fluorine has also been detected in some varieties of bone and in the enamel of teeth. No compound of fluorine with oxygen, or chlorine, has yet been satisfactorily shown to exist*. According to Dr. Leeson (*Mem. Ch. Soc.*) *fluoride of iodine* may be obtained by passing the gas generated from 1 part of peroxide of manganese, 3 of pure fluor spar, and 6 of concentrated sulphuric acid, mixed in a leaden vessel, through water in which iodine is diffused: crystalline scales resembling iodide of lead are deposited. *Fluoride of bromine* similarly obtained does not crystallize.

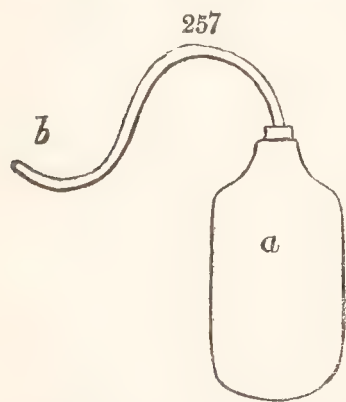
It may be remarked of the bodies which have been above described, that although they do combine with each other, they are not possessed of powerful mutual affinities; and, consequently, their compounds are, with few exceptions, either unstable or easily decomposed; this is what might be expected as a consequence of their analogous electrical relations; for they are all apparently evolved at the anode in voltaic arrangements. Yet, in respect to each other, it has been supposed that they may exhibit opposite, though feeble electrical energies, and that such compounds, in voltaic decomposition, may thus present one of their elements at the negative electrode; a mixed solution, for instance, of bromine and iodine, when electrically decomposed, is stated to evolve bromine at the positive, and iodine at the negative surface, and it has hence been concluded, that iodine is electro-positive in respect to bromine; but the possible influence of secondary electro-chemical action, in these cases, has not been taken into the account, and the statements are quite at variance with the well-established laws of electro-chemical decomposition. The compounds of the bodies above described with hydrogen and with the metals, when subjected to electrical decomposition, give up the inflammable body at the negative pole, or cathode, while the supporter of combustion appears at the positive pole, or anode.

* Baudrimont (*Journ. de Chim. Med.*, xii., 374,) and the Messrs. Knox, have each published experiments by which they state that fluorine may be isolated. (*Phil. Mag.*, 3rd Series, vol. ix. x. and xii.) "But more

than one skilful chemist of name has been less fortunate in obtaining indications so decisive, of the isolation of fluorine." (GRAHAM.)

§ VI. HYDROGEN. H. 1.

HYDROGEN was first duly examined in a pure state by Mr. Cavendish, in 1766. (*Phil. Trans.*, vol. LVI. 144.) It had before been confounded with several of its compounds, under the name of *inflammable air*: the term *hydrogen* was given to it by the French chemists in consequence of its being one of the elements of water (from $\upsilon\delta\omega\rho$, *water*, and $\gamma\epsilon\rho\nu\epsilon\iota\nu$, *to generate*). It also forms a component of all vegetable and animal products, and is therefore abundantly diffused throughout nature.



Hydrogen gas may be obtained by the action of iron or zinc upon dilute sulphuric acid. Some nails, or pieces of iron wire, or fragmented or granulated zinc, may be introduced into the tubulated flask *a* (fig. 257), and covered with sulphuric acid diluted with six or eight times its bulk of water; an effervescence ensues, heat is evolved, and the gas escapes by the bent tube *b*, (inserted by grinding into the neck of the flask,)

and may be collected in the hydro-pneumatic apparatus. ($\text{SO}_3, \text{HO} + \text{Zn} = \text{SO}_3, \text{ZnO} + \text{H}$.) The hydrogen, however, which is thus obtained, is never perfectly pure. When procured by the means of iron, its odor is peculiar and disagreeable, in consequence, according to Berzelius, of its containing a portion of volatile oil, formed by its union with a minute quantity of carbon, which all common iron contains. When such gas is passed through alcohol, much of the odor is absorbed by it, and on diluting it with water, it becomes milky. Obtained by means of zinc, the gas is perhaps somewhat more pure, but it appears to hold a trace of zinc and of carbon in solution, and perhaps in some cases traces of sulphur and of arsenic*. For the purposes of delicate experiments, hydrogen must be passed through a solution of potassa, and then dried by passing it through a tube containing fragments of fused chloride of calcium; it should also be collected over mercury, and procured from purified zinc, and pure sulphuric acid so far diluted as to act but slowly upon the metal.

* The common zinc of commerce is here alluded to; pure zinc is very slowly acted on by dilute sulphuric acid: indeed, we sometimes find commercial zinc so pure as to yield hydrogen very tardily. According to Dumas, (*Recherches sur la Composition de l'Eau*, *Ann. Ch. et Ph.*, Juin, 1843,) the impurities of hydrogen derived from the zinc and sulphuric acid of commerce are oxides of nitrogen, sulphurous acid, and arsenuretted and sulphuretted hydrogen: the nitrous oxides are derived from impure sulphuric acid, and when it has been attempted to get rid of these by a current of sulphurous acid, the latter is carried over with the hydrogen: arsenuretted and especially sulphuretted hydrogen almost always occur; so that where pure hydrogen is required, pure sul-

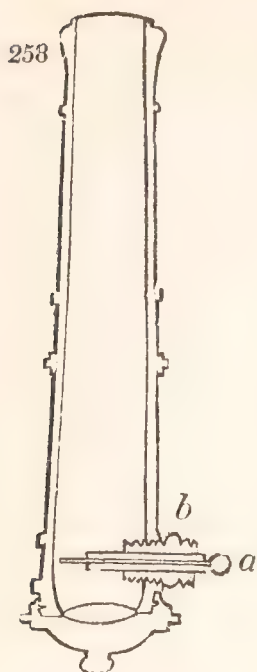
phuric acid and water must be used, and the gas subjected to reagents capable of abstracting all traces of sulphuretted and arsenuretted hydrogen: a solution of nitrate of lead arrests the former, and of sulphate of silver the latter. The gas, therefore, should be conducted through **U** tubes filled with pounded glass so as to extend the surface of the metallic solutions, and thence through similar tubes containing fragments of pumice imbued with concentrated solution of potassa, pieces of common potassa, and of caustic potassa which has been fused at a red heat: lastly, it must be dried by passing it through a tube containing fragments of pumice imbued with oil of vitriol and surrounded by ice. (See also upon this subject, JACQUELAIN, *Ann. Ch. et Ph.*, Février, 1843.)

The hydrogen liberated by the voltaic decomposition of water by platinum surfaces (see WATER), may, when dried, be considered as pure. Upon the same principle it may be obtained by inverting a platinum crucible in dilute hydrochloric acid, and placing a plate of zinc upon it; the hydrogen is then evolved by the voltaic action of the two metals, and a portion of it collects within the crucible. This gas is also pure when liberated from pure water by the action of an amalgam of potassium or of sodium.

Hydrogen is an uncondensable aëriiform fluid; it is not absorbable by water, unless that liquid has been previously deprived, by long boiling, of common air, in which case 100 cubic inches dissolve about 1·5 cubic inches of the gas. It has no taste, and when perfectly pure, is inodorous; but it usually has a slight disagreeable smell. It has great power of refracting light (p. 92.) It may be respired for a short time, though it is instantly fatal to small animals. M. Maunoir, after having breathed a quantity of pure hydrogen, found that his voice had become remarkably shrill. (*Phil. Mag.*, iv. 214.) The intensity of sound is greatly diminished in an atmosphere of hydrogen; Leslie, indeed, found it more feeble than its rarity compared with air would have led him to expect. He placed a piece of clock-work by which a bell was struck every half minute under the receiver of the air-pump, and, after exhausting the air, filled the receiver with hydrogen; but the sound was then even feebler than in the highly-rarefied atmosphere. (*Ann. Philos.*, 2nd Series, iv. 172.) It is stated that sound moves at least three times as fast in hydrogen as in air.

Hydrogen gas is the lightest known form of matter, and its equivalent, combining, or atomic weight, is below that of all other substances; it is, therefore, conveniently assumed as *unity* in reference to the *atomic weights* of all other bodies. In consequence of its extreme lightness, it is difficult directly to determine its weight with accuracy by the common process; but the researches of Berzelius and Dulong, and of Dr. Prout, lead us to infer that its specific gravity, compared with oxygen, is as 1 to 16: 100 cubic inches, therefore, of pure hydrogen gas at mean temperature and pressure weigh only 2·1483 grains, and compared with air, its specific gravity would be nearly as 7 to 100, or more correctly as 0·0694 to 1. (Berzelius and Dulong's determination gave 0·0687 to 0·0688; but Bous-singault and Dumas have shown that these numbers are too low, and give the density of hydrogen as between 0·0691 and 0·0695. *Ann. Ch. et Phys.*, 3rd Series, viii. 201.) At the temperature of 32° 100 cubic inches weigh 2·22756 grains. (THOMSON.)

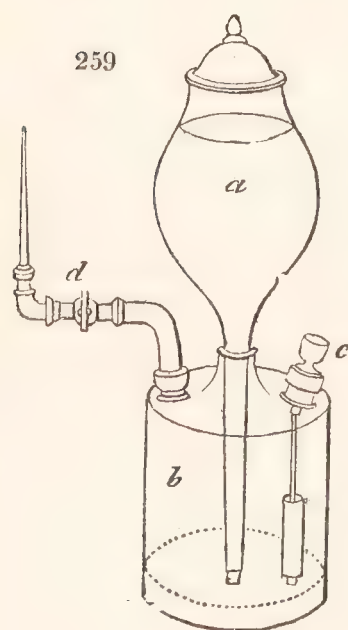
The low specific gravity of hydrogen is well and amusingly illustrated by substituting it for common air, in soap bubbles, which then rapidly ascend in the atmosphere, and may be kindled by the flame of a taper. The same circumstance also led to its employment for the inflation of balloons, which, however, have of late years been generally filled with coal-gas. Small balloons may be purchased, made of gold-beater's skin, or of the lining membrane of the crop of a turkey, which, when filled with pure hydrogen, rise to the ceiling, their specific gravity being inferior to that of the surrounding air. Some of these when filled with hydrogen, do not weigh more than 42 grains, while the same bulk of air would weigh 52 grains, so that their buoyant power is about = 10 grains.



Hydrogen is inflammable, and extinguishes flame. When pure, it burns quietly, with a pale yellowish flame at the surface in contact with air; but, if mixed with thrice its volume of air, it burns rapidly, and with detonation. In making this experiment, a strong phial, capable of holding about six ounces of water, may be employed; or the *inflammable air-pistol*, which admits of the mixture being fired by the electric spark. This instrument consists of a cylinder of brass, about three-fourths of an inch diameter, and six inches long, in the form of a small cannon or pistol-barrel, properly mounted and having a wire, *a* (fig. 258), at the part usually occupied by the touch-hole, passing through a tube of ivory, *b*, and not quite touching the interior of the cylinder; an electric spark communicated to this wire inflames the mixture of hydrogen and atmospheric

air in the interior. It may be charged, by previously filling it with dry sand, and emptying it out into a phial of hydrogen, which then rises into the gun sufficiently mixed with air; the muzzle may be secured by a cork, which is expelled with much violence and a loud report, upon the inflammation of the gas.

The electrical air-gun may also be charged, by holding it for a moment over the open jet of the following instrument, (fig. 259,) always taking care that there is a due admixture of atmospheric air, otherwise the electric spark will not inflame it. *a* is a funnel-shaped vessel, fitting by a ground-joint into the three-necked bottle *b*; to the stopper *c* is annexed a brass wire, with a cylinder of zinc screwed upon its lower end; *d* is a tube furnished with a stopcock and jet-pipe; the capacity of the vessel *a* should be



nearly equivalent to that of *b*, and may contain from one to three or four pints. To charge this apparatus with hydrogen, *b* is three-fourths filled with water, and the stopper *c* being removed, a quantity of sulphuric acid, previously diluted with its bulk of water, is poured in by the long funnel, so that it may remain at the bottom of the water which now fills the vessel. The stopper *c*, with its appended piece of zinc, is then put in, and the generated hydrogen forces the dilute acid into *a*, where its pressure serves to propel the gas through *d*, whenever the stop-cock is opened; the acid, at the same time descending, produces a fresh portion of hydrogen by again acting upon the zinc. This instrument is useful where small quantities of hydrogen are required for burning, charging air-guns, and other purposes.

It will be found that hydrogen during combustion combines with eight times its weight of oxygen: and according to Despretz, the heat thus evolved by the combustion of a pound of hydrogen (in common air) is sufficient to raise the temperature of 236.4 pounds of water from 32° to 212°.

Volta's air-lamp, in which a jet of hydrogen is inflamed by a small spark from an electrophorus, also furnishes an elegant illustration of the ready inflammability of hydrogen by the electric spark.

In examining into the quantity of atmospheric air required to form an explosive mixture with hydrogen, Mr. Cavendish found the loudest report was produced by one volume of hydrogen with three of air. One of hydrogen with nine of air burned very feebly, and four of hydrogen with one of air burned without explosion. (*Phil. Trans.*, LVI.)

If, instead of a mixture of hydrogen and atmospheric air, two volumes of hydrogen mixed with one of *oxygen* be burned in the electrical air-gun, or inflamed in a stout and small phial, the explosion is extremely violent; but if the mixture be diluted with eight measures of hydrogen, or with nine of oxygen, it no longer explodes.

The inflammability, as well as the low specific gravity of hydrogen, are shown in the following experiments:—Let a jar filled with this gas stand for a few seconds, with its open mouth upwards; on letting down a candle, the gas will be found to have escaped, and to be replaced by common air. Place another jar of the gas inverted, or with its mouth downwards; the gas will now be found to remain a much longer time in the jar, being prevented from escaping upwards by the bottom and sides of the vessel. Provide an air-jar, with a stop-cock and jet, and fill it with hydrogen, upon the shelf of the pneumatic trough; then set fire to the gas at the jet, and immediately lift the jar out of the water, and hold it firmly by the brass cap. The flame will continue for some time at the jet, the hydrogen being propelled through it by the pressure of the external air; but when the air becomes mixed in such proportion with the gas as to form an explosive mixture, the flame recedes through the jet, and the whole kindles suddenly. (BERZELIUS.) Hydrogen may in fact be decanted, as it were, *per ascensum*, from one jar into another held above it. Thus, if a light bell-glass be suspended with its mouth downwards to one end of a scale-beam, and accurately counterpoised, it will be found, on placing a jar of hydrogen gas closed by a plate of glass underneath it, that the hydrogen, on removing the glass plate, will ascend into the bell, and by its lightness, cause the counterpoise to sink; the hydrogen may afterwards be inflamed by a taper introduced into the counterpoised bell.

If a current of hydrogen be inflamed when issuing from a small aperture, and a tube of eighteen or twenty inches in length be held over the flame, as in fig. 260, a peculiar musical tone is produced, varying in its pitch with the length and diameter of the tube, and the extent to which the flame, which should be very small, is introduced within it. This effect is not peculiar to hydrogen, but is produced by a variety of other flames (FARADAY, *Journal of Science and the Arts*, vol. v.), and is referable to the regular succession of little explosions and consequent vibrations produced by the combustion of the gas in the tube.

The tendency which gaseous fluids have to become completely mixed under all circumstances, and as it were to penetrate each other, is well illustrated where hydrogen is employed. Thus, if two small phials, the one containing oxygen and the other hydrogen, be connected perpendicularly by a long glass tube, of small bore, it will be found, that although the hydrogen



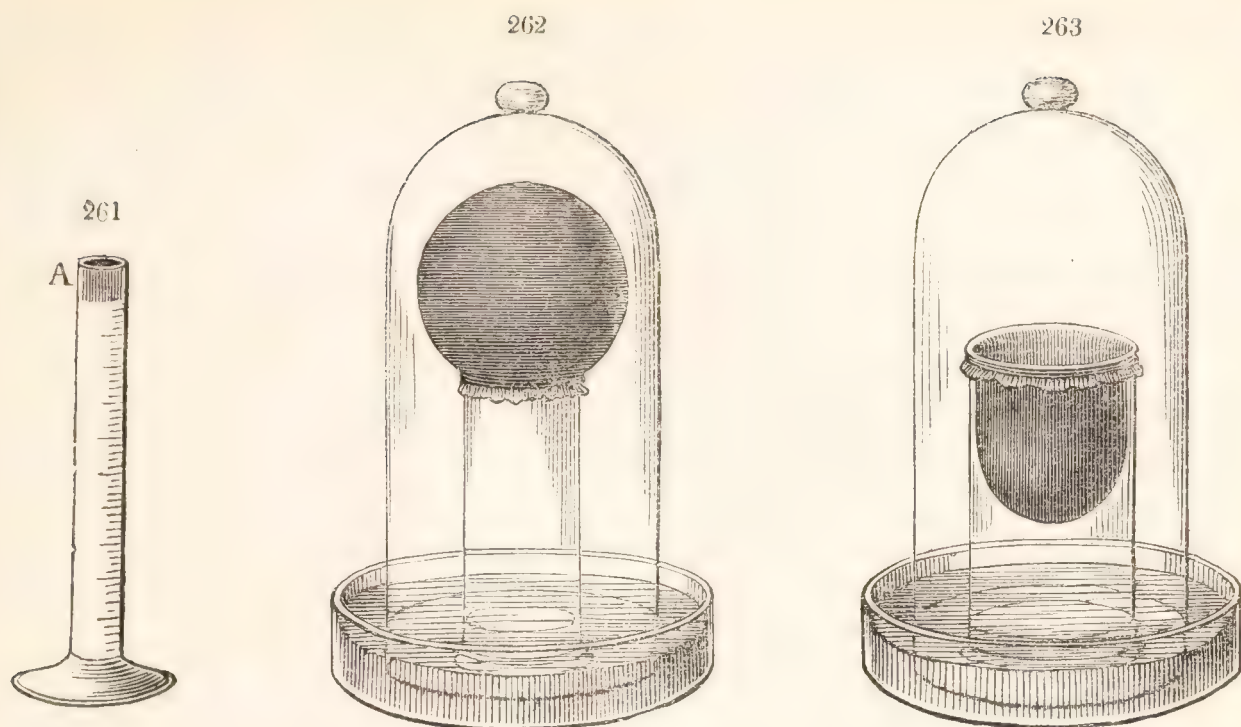
be uppermost, and much lighter than the oxygen, it will, in the course of a few hours, have perfectly mixed with the oxygen, and the gases will be found in equal proportions in both phials; hence the expression that one gas acts as a vacuum with respect to another. (DALTON, *Manchester Memoirs*, vol. i., New Series.)

The facility, too, with which hydrogen passes through crevices, fissures, and capillary tubes, as also through membranes and various organic tissues, is very remarkable. Attention was first called to this subject by a curious observation of Döbereiner on the escape of hydrogen through a small crack or fissure in a glass jar, which had been filled with the gas, and placed upon the shelf of the pneumatic trough; to his surprise, the water rose in the jar nearly three inches above the level of that in the trough. The subject was afterwards investigated by Professor Graham, (*Edinburgh Philos. Trans.*, xii. 222.) The following is an abstract of his inquiries, abridged from his *Elements of Chemistry*.

On examining Döbereiner's result, he found that while the hydrogen escaped outwards, a portion of air penetrated inwards, amounting to between one-fourth and one-fifth of the volume of the lost hydrogen: that, in fact, when hydrogen communicates with air by such a chink, there is a powerful disposition to mutual intermixture; "a particle of air, however, does not interchange with a particle of hydrogen of the same magnitude, but of 3·83 times its magnitude. We may adopt the word *diffusion-volume* to express this diversity of disposition in gases to interchange particles, and say that the diffusion-volume of air being = 1, that of hydrogen gas is = 3·83. Now every gas has a diffusion-volume peculiar to itself, and depending upon its specific gravity; of those gases which are lighter than air, the diffusion-volume is greater than 1, and of those which are heavier, the diffusion-volume is less than 1."

Professor Graham's results were obtained by what he calls a *diffusion-tube*; it is a graduated glass tube of about half an inch diameter, and fourteen inches long; one end is closed by a plate of plaster of Paris of about one-fifth of an inch thick; it may be used over mercury or water, but in the latter case care must be taken in filling it, to keep the plaster plug dry. Fig. 261 represents a good form of diffusion-tube; it is graduated into 100 parts, and closed at *a* by a plug of plaster of Paris. It should be filled with hydrogen or other required gas, by propelling it from a jet into the tube, so as thoroughly to displace the atmospheric air without wetting the plaster stopper, and then transferred to a basin of water: in this case the gas diffuses into the atmosphere through the pores of the stucco, the water rises proportionately in the tube, and in about half an hour, the whole of the hydrogen will have escaped, and a certain quantity of common air entered: in experiments for determining the proportion of gas diffused and of replacing air, inequality of pressure must be guarded against by placing the diffusion-tube in a jar of water which must be filled up in proportion as it rises in the tube, and the inner and outer levels kept equal. Assuming the diffusive power of air as = 1, that of hydrogen is = 3·8; of oxygen = 0·9; of nitrogen = 1·014.

Cork, spongy platinum, and other porous substances, may be substituted for the stucco, in the diffusion-tube; or a piece of bladder, or thin caoutchouc, may also occasionally be used. With the latter a very striking experiment, illustrative of this form of *endosmose* and *exosmose*, may



be made as follows:—confine a portion of common air in a tumbler or wide-mouthed jar, by tying it carefully over with a piece of thin sheet-caoutchouc, and place it under a large bell-glass filled with hydrogen gas, and standing in a dish of water: the hydrogen will gradually find its way through the caoutchouc and act upon it with such elastic power as forcibly to distend and even ultimately burst it (fig. 262.) If the included jar be filled with hydrogen, and the bell-glass with air, an opposite result will ensue, as shown by the concave instead of convex surface assumed by the elastic diaphragm. (fig. 263.)

If a thin flaccid bladder, containing common air, be suspended in a jar of carbonic acid, it will become distended to the utmost by the entrance of the carbonic acid from without: or if the bladder distended with carbonic acid be suspended in the air, it will become flaccid, in consequence of the exosmose of the former prevailing over the endosmose of the latter. Where the membranes are moist, the water by its solvent power may tend to facilitate the transfer of gases; this diffusive power, for instance, of carbonic acid depends upon the intervention of a moist membrane.

It has been shown that gases flow into a vacuum with velocities which are inversely as the square roots of their densities; that is, with velocities corresponding to the numbers which express their diffusion-volumes: hence the law of diffusion has been regarded (T. S. THOMSON, *Phil. Mag.*, 3rd Series, iv. 321) as confirming Dalton's theory, that gases are inelastic towards each other; a conclusion, however, which Graham hesitates to adopt. (*Elements of Chemistry*, p. 75.)

In discussing the nature of flame and the causes of their luminosity and heat (p. 127,) I have alluded to the high temperature of that of hydrogen: it is occasionally employed for exciting intense heat; and, when mixed with oxygen, and burned as the mixture issues from a small jet, it excites a temperature nearly equal to that of the arc of flame in the voltaic circuit. A blow-pipe upon this construction was first made by Newman, and afterwards improved, as to its safety, by Professor Cumming, of Cambridge. (*Journal of Science and the Arts*, i. 65, and ii. 380.) A full account of the construction and use of this hydro-oxygen blow-pipe will be found in Dr. Clarke's book upon the subject. (London, 1819.) Hemming's safety-tube may also be used in these

experiments. (See *Phil. Mag.*, 3rd Series, i. 82.) An excellent mode of obtaining intense heat by the combustion of oxygen and hydrogen, consists in propelling them from separate air-holders through a burner composed of two concentric tubes: a good form of such a burner has been described by Daniell. (*Phil. Mag.*, 3rd Series, ii. 57.) The apparatus for this purpose has also been further improved by Maugham, especially as relates to its application to the solar microscope. (*Trans. Soc. Arts, &c.*, vol. L.) It may be observed, that in this and similar cases where the inflammable gas is mixed with oxygen, the nature of the flame is materially altered, the combustion being entire throughout the body of the flame, and not limited to the film in contact with air, as represented at p. 128. So that in the former case the quantity of the combustible consumed in a given time, and the quantity of oxygen combining with it in a given time, are greatly increased.

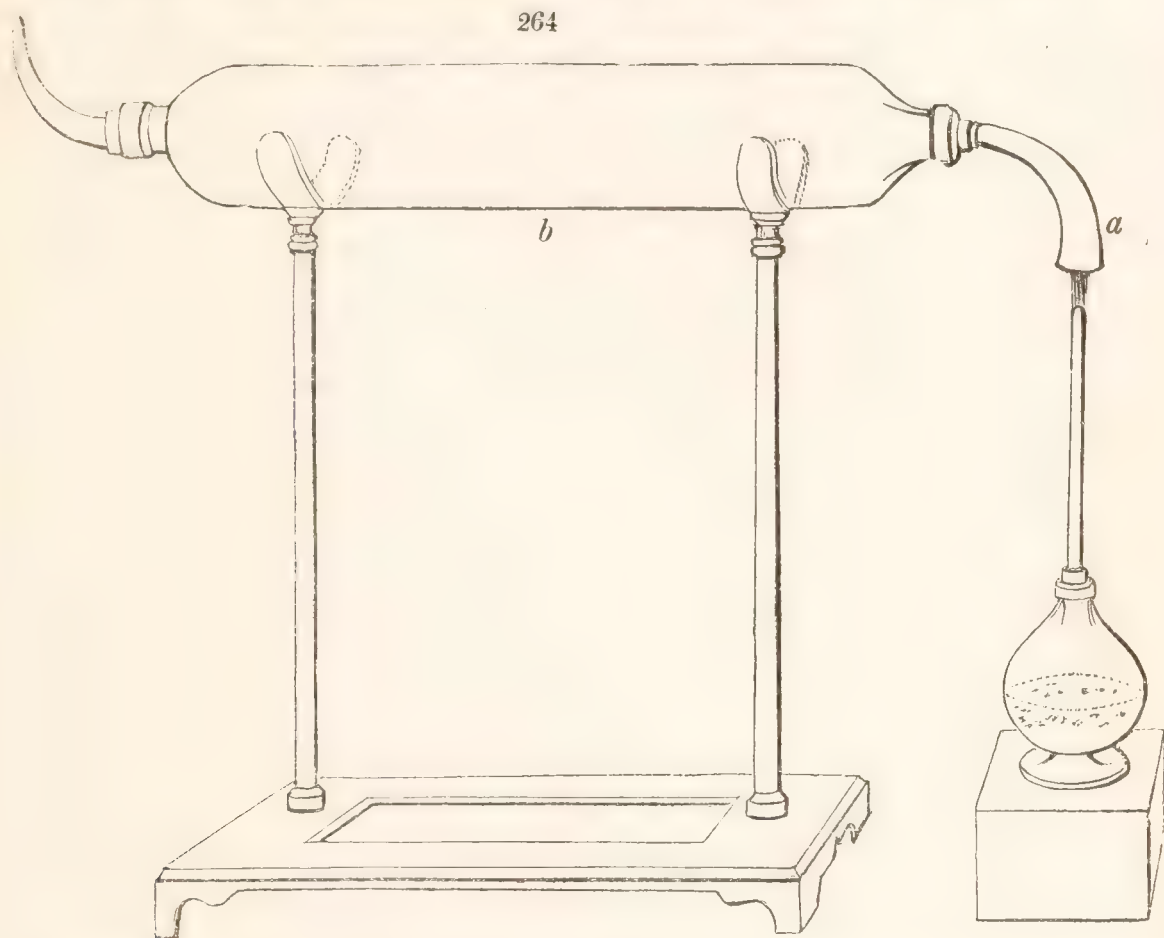
HYDROGEN AND OXYGEN. WATER. PROTOXIDE OF HYDROGEN. HO, or H, or Aq. Water was long regarded as an element, and was supposed convertible into earth, until Lavoisier in 1773 showed the fallacy of that notion. Cavendish, and Watt, in 1781, demonstrated the production of water by the combustion of oxygen and hydrogen, and the former, to whom the important discovery of the composition of water is strictly due, proved the correspondence in weight of the resulting product with that of the gases used in its formation. Lavoisier first resolved water into its constituents, and Von Humboldt and Gay Lussac proved that the volume of the oxygen to the hydrogen was exactly as 1 : 2. The relative weights of those gases were carefully determined by Berzelius and Dulong, and shown to be very nearly as 88·9 : 11·1.

When *two volumes* of pure hydrogen gas are mixed with *one volume* of pure oxygen gas, and the mixture inflamed in a proper apparatus by the electric spark, they totally disappear, and water equal in weight to the gases consumed is formed: and again, if water be exposed to electrolytic action, it is resolved into *two volumes* of hydrogen, disengaged at the negative pole or cathode, and *one volume* of oxygen, disengaged at the positive pole or anode (see p. 216); so that water is thus proved by *synthesis*, and by *analysis*, to consist of two volumes of hydrogen, combined with one volume of oxygen. The specific gravity of hydrogen, compared with oxygen, is as 1 to 16; these numbers, therefore, represent the comparative weights of equal volumes of those gases; but as water consists of *one volume of hydrogen and half a volume of oxygen* it is obvious that the relative *weights* of those elements will be as 1 : 8. (These numbers are deduced from Dr. Prout's researches, and their perfect accuracy has more recently been determined by the elaborate investigations of Dumas. *Récherches sur la Composition de l'Eau. Ann. Ch. et Ph.*, Juin, 1843.)

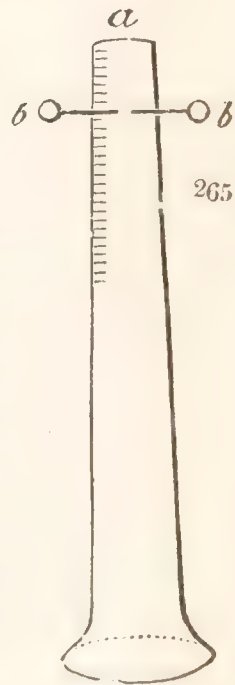
	Atoms		Weights.		Per Cent.		Volumes.
Hydrogen	1	1	11·1	1·0
Oxygen	1	8	88·9	0·5
<hr/>							
Water	1	9	100·0		

The experiments illustrating the composition of water, and showing the proportions in which its elements are united, may be divided into *synthetic* and *analytic*. Among these the following may be selected:—

Synthetic Experiments.—(1.) Burn a current of hydrogen under the copper funnel *a*, represented in the following wood-cut, fig. 264; by uniting with the oxygen of the atmosphere it will produce aqueous vapour, which passing into the glass cylinder *b*, will condense in drops*.

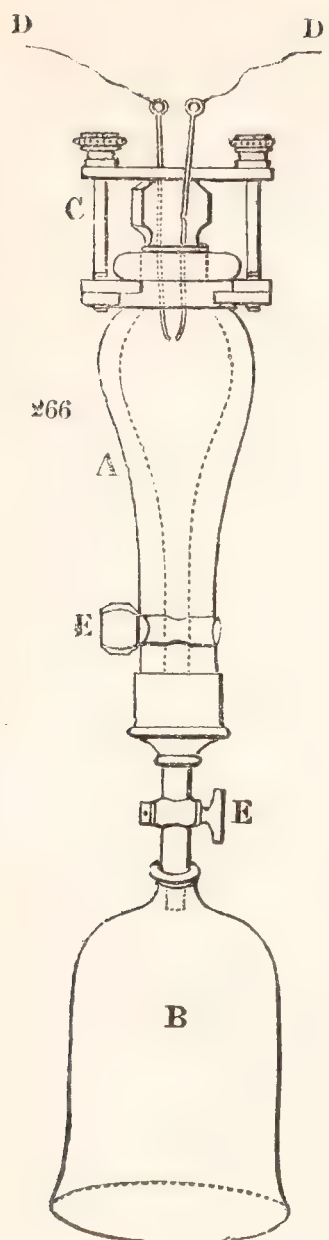


(2.) If two measures of pure hydrogen be mixed with one of pure oxygen, and detonated in the graduated glass tube *a*, fig. 265, standing over water or mercury, by an electric spark passed through the platinum wires *b b*, the gases disappear. If there be any excess of either of the gases, the portion in excess will remain unconsumed. At the moment the explosion takes place the gaseous mixture becomes greatly expanded, probably to fifteen times its original bulk (DAVY on *Flame*, p. 90), and a portion is apt to escape at the bottom of the tube; hence the advantage of performing the experiment over mercury in the form of apparatus recommended by Dr. Ure. (See EUDIOMETER.)



(3.) The same experiment may be thus varied. A (fig. 266) is a strong and thick glass vessel provided with a glass stop-cock *E*, and with a ground stopper firmly secured by the brass collar *c*, through which the platinum wires *D D* pass. The vessel *A*, previously exhausted of air, is placed upon the bell-glass *B*, in the pneumatic trough, containing a mixture of pure oxygen and hydrogen in the above-mentioned proportions. Upon opening the stop-cocks *E F*, a quantity of the mixed gases passes into *A*, where, *after having carefully closed the stop-cocks*, it may be inflamed by an electric spark passed through the platinum wires. At the instant of the detonation, a

* On examining the water thus produced, it is generally slightly acid from the presence of nitric acid, derived from the nitrogen in the atmosphere; if hydrogen be in excess it sometimes contains ammonia. (SAUSSURE, *Ann. de Chim.*, LXXI. p. 282.)



vivid flame pervades the upper vessel, and it becomes lined with moisture. If the stop-cocks be again opened, a fresh portion of the mixed gases enters, and may be inflamed as before.

(4.) A mixture of oxygen and hydrogen gases, suddenly submitted to violent mechanical compression, unite with combustion, and produce water. (BIOT.) Under a more gradual compression, equivalent to that of 50 atmospheres (by sinking the mixed gases in a tube, sealed by mercury, to a depth of 540 metres in the sea), the gases do not unite. (DELAROCHE.) Water may also be produced by heating the mixed gases to a temperature below that required for their combustion with flame. (DAVY on *Flame*, p. 68.) According to Grotthus, no explosion takes place by an electric spark, in a mixture of two volumes of hydrogen and one of oxygen, expanded to six times its volume by heat, or to sixteen times its volume by diminished pressure. (*Ann. de Ch.*, LXXXII.) Electric sparks, however, passed for some time through such a mixture, gradually produce water. A red heat, visible by daylight, inflames the mixture; but a very dull red heat only causes the combination of the gases without explosion. Graham states, that if a mixture of oxygen and hydrogen be heated in a vessel containing a quantity of pulverised glass, or any sharp powder,

they begin to unite, in contact with the foreign body, in a gradual manner, without explosion, at a temperature not exceeding 660° .

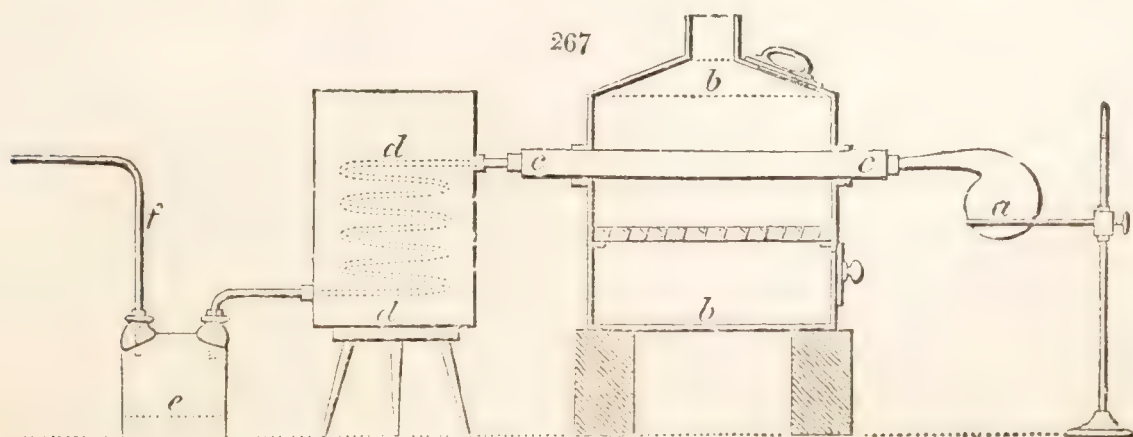
(5.) A discovery, connected with the present subject, was made in the year 1824, by Döbereiner, who found that spongy platinum, (see PLATINUM,) possessed the singular property of causing the immediate combination of hydrogen and oxygen, with heat sufficient to inflame the gases, and of course to render the metal red-hot, the phenomena being analogous to those previously observed by Davy in his researches on combustion without flame (see p. 129). If a small piece of well prepared spongy platinum be held in a jet of hydrogen issuing from a small tube into the atmosphere, it immediately becomes hot enough to inflame the gas. If a mixture of oxygen and hydrogen, or of atmospheric air and hydrogen, not in explosive proportions, be submitted to the action of the platinum, it disposes the gases to slow combination, water is gradually formed, and if there be a sufficiency of oxygen, the whole of the hydrogen disappears under its influence; if, on the other hand, there be excess of hydrogen, the oxygen disappears. In analyzing certain gaseous mixtures, therefore, platinum, in this peculiar state of mechanical division, becomes a valuable agent. For more convenient application to such purposes, the platinum may be mixed with an equal weight of pure clay, and moulded with a little water into small balls, which must be carefully dried at a high heat. These may be conveniently thrown up into gases standing over mercury, and their power is not impaired by use; for they may always be rendered efficient, or their power restored, by heating them

red-hot. Spongy platinum also causes the union of oxygen with several other gases, such as with carbonic oxide, and, at high temperatures, with olefiant gas; it also promotes the decomposition of nitric oxide by hydrogen. (DULONG and THENARD, *Ann. de Ch. et Ph.*, xxiii. 440.) It is an essential condition in all cases of the catalytic influence of platinum that its surface should be absolutely *clean*, the slightest film of foreign matter impairing or in some cases preventing the action: hence the advantage derived from carefully heating spongy platinum, which has become inert, in a clear flame. A very few other metals operate in the same way, but less perfectly than platinum, such as palladium and iridium. Gold and silver in fine leaves are efficient at temperatures above 212° . (See, in reference to these *catalytic* actions, a paper by REISET and MILLON, *Ann. Ch. et Ph.*, July, 1843; also, L. GMELIN'S *Handbuch*, I. Art. *Wasserbildung*.)

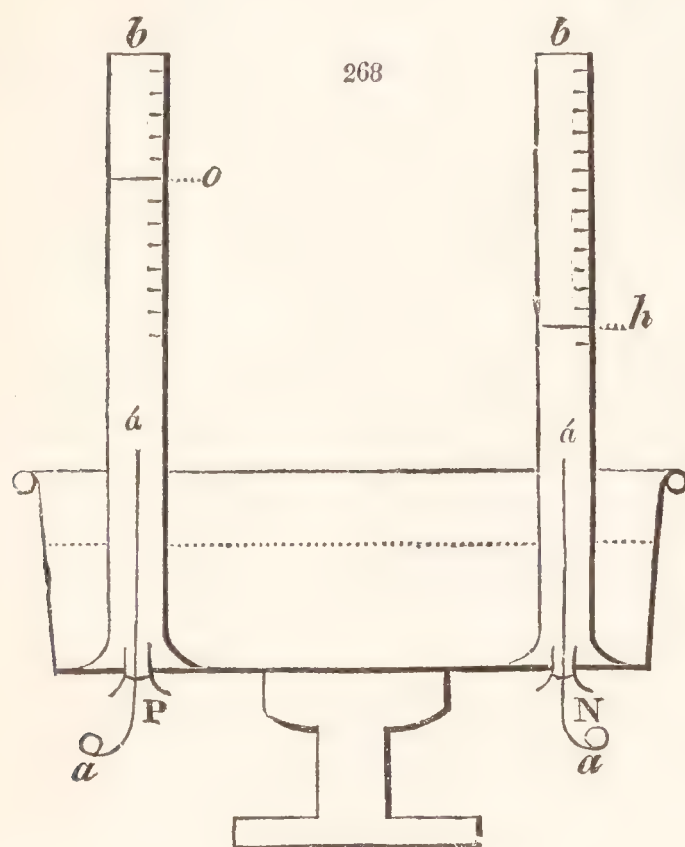
(6.) The effects observed by Faraday respecting the action of the platinum which had formed the positive pole of the voltaic pile upon a mixture of oxygen and hydrogen gases, and which he has detailed and investigated in the sixth Series of his *Experimental Researches in Electricity*, (*Phil. Trans.*, 1834, p. 55,) are apparently of the same nature as those observed by Döbereiner. He refers them to a peculiar attraction between the *perfectly clean* metallic surface and the particles of the gaseous mixture, resembling that by which bodies become *wetted* by fluids with which they do not combine chemically, or in which they do not dissolve; or the attraction which renders certain bodies hygrometric, though they neither dissolve in, nor combine with, water; or lastly, to a kind of attraction analogous to that between air and glass, so well known to barometer-makers. It may be conceived that by some such attractive force the particles of the oxygen and hydrogen become so approximated, and deprived of their gaseous repulsion, as to enter into chemical combination, and in so doing to evolve the heat which raises the temperature of the metal.

Analytic Experiments. Water may be decomposed or resolved into its elements, by a variety of processes, of which the following will suffice for our present illustration:

(1.) *a* (fig. 267) is a glass retort, into which is introduced a given weight of water; *b b* a small furnace through which passes the porcelain tube *c c*, which terminates in the spiral pewter tube *d d*, immersed in water. A given weight of pure iron wire, coiled up, is introduced into the tube *c*, and the whole made red-hot; the water in *a* is then made to boil, and the vapor, on coming into contact with the red-hot iron, is in part decomposed; the oxygen is retained by the iron; and the hydrogen, escaping through the tube *f*, may be collected as usual. Any unde-



composed portion of water is condensed in the worm-pipe *d*, and drops into the vessel *e*. After this experiment the iron will be found to have increased in weight; and if attention be paid to the quantity of water which has collected in *e*, and to the weight of the hydrogen gas evolved, it will be found that the weight gained by the iron, added to that of the hydrogen, will be equal to the weight of the water which has disappeared.



platinum, *a' a'*, which rise up into, and over which are inverted, the tubes *b b*, also filled with water. The wires are now connected with a moderately-powerful voltaic apparatus: oxygen is evolved at the positive and hydrogen at the negative electrode, which gases rise into the tubes, and it is seen that one volume of oxygen, *o*, and two volumes of hydrogen, *h*, are the constant results*. If these gases be mixed and detonated, pure water is again formed. In employing this apparatus the conducting

Lavoisier concluded, from an experiment thus conducted, that water consisted of 85 parts by weight of oxygen, and 15 by weight of hydrogen: that is, that for every 15 grains of hydrogen gas evolved, 85 grains of oxygen were condensed by the iron.

(2.) Decomposition by voltaic electricity best illustrates the composition of water, since it exhibits both the oxygen and hydrogen in the gaseous form. The annexed cut represents a section of an apparatus for this purpose. It is a glass vessel containing water, having two wires of platinum, *a a*, passing through its bottom, which terminate in two narrow plates or strips of

* By passing electric discharges from a Leyden jar by two fine wires through water, oxygen and hydrogen are evolved at both; the decomposition, therefore, is apparently not electro-polar. In the electrolysis of water, as described in the text, the bubbles of hydrogen are larger and rise more regularly than those of oxygen, which are much more minute and diffused; a deficiency in the oxygen is also occasionally remarked, which, when the proportion of sulphuric acid added to improve the conducting power of the water exceeds that above mentioned, is sometimes considerable: it probably arises from the solution of a portion of the oxygen in the dilute acid, or from the formation of oxy-water. Mr. Faraday recommends for the Voltameter (p. 228), an acid of the specific gravity of 1.3. From a mixture of two measures of sulphuric acid and one of water he obtained 42 volumes of hydrogen and

only 12 (instead of 21) of oxygen. (*Researches*, vii., § 728.) On the subject of the peculiar odor perceptible during the electrolysis of water and the production of ozone, see also Schönbein, *Poggend.*, 1. 616.

If the water used for voltaic decomposition be not pure, its impurities are shown by the production of acid and alkaline matter at the positive and negative pole. But pure water is so imperfect an electrolyte that, in the above experiment, it is convenient to render it more easy of decomposition by the addition of a little sulphuric acid. (See page 216, and note.) In using any apparatus, such as the volta-meters, in which water is decomposed by platinum electrodes, care must be taken that no part of the clean electrode be exposed to the evolved gases, as it will tend to induce their recombination, and in so doing sometimes become red-hot and cause explosion.

power of the water requires to be augmented by the addition of about a tenth part of sulphuric acid.

Properties of Water. Water, in its ordinary state, such as *spring* and *river water*, is always so far contaminated with foreign substances as to be unfit for many chemical purposes, and frequently, as will be more fully shown hereafter, even for domestic use. *Rain-water* is much more pure, but it always contains small quantities of carbonic acid and of atmospheric air, besides appreciable traces of ammonia and of vegetable or animal matter; to the latter it owes its property of becoming putrid when kept. Hassenfratz asserts that snow-water contains excess of oxygen (*Jour. de l'Ecole Polytech.*, cap. iv., 570.) Rain-water collected near the sea shows traces of chlorine. The distinction of water into *hard* and *soft* has reference to its less or greater purity.

The following table shows the solid contents of the water of the Thames and of the New River, together with that of the Colne and the Lea.

ANALYSES OF THE WATER OF THE THAMES, NEW RIVER, COLNE, AND THE LEA.

1 Imperial Gallon = 10lbs. = 70,000 grs. contains	THAMES. (Phillips and Bostock.)			NEW RIVER. (Phillips.)	COLNE. (Phillips.)	LEA. (Phillips.)		
	Westminster. grs.	Brentford. grs.	Above Teddington. grs.	grs.	grs.	grs.		
Carbonate of lime	16·4	16·5	14·8	14·7	18·1	18·		
Sulphate of lime	6·	} 2·7	1·2	1·6	} 3·2	1·8		
Chloride of sodium....	2·		1·4	1·7		1·5		
Oxide of iron.....	} traces	traces	traces	traces	} traces	traces		
Silica				1·2		2·4		
Magnesia				traces		traces	traces	} traces
Organic matter								
	<hr/> 24·4	<hr/> 19·2	<hr/> 17·4	<hr/> 19·2	<hr/> 21·3	<hr/> 23·7		

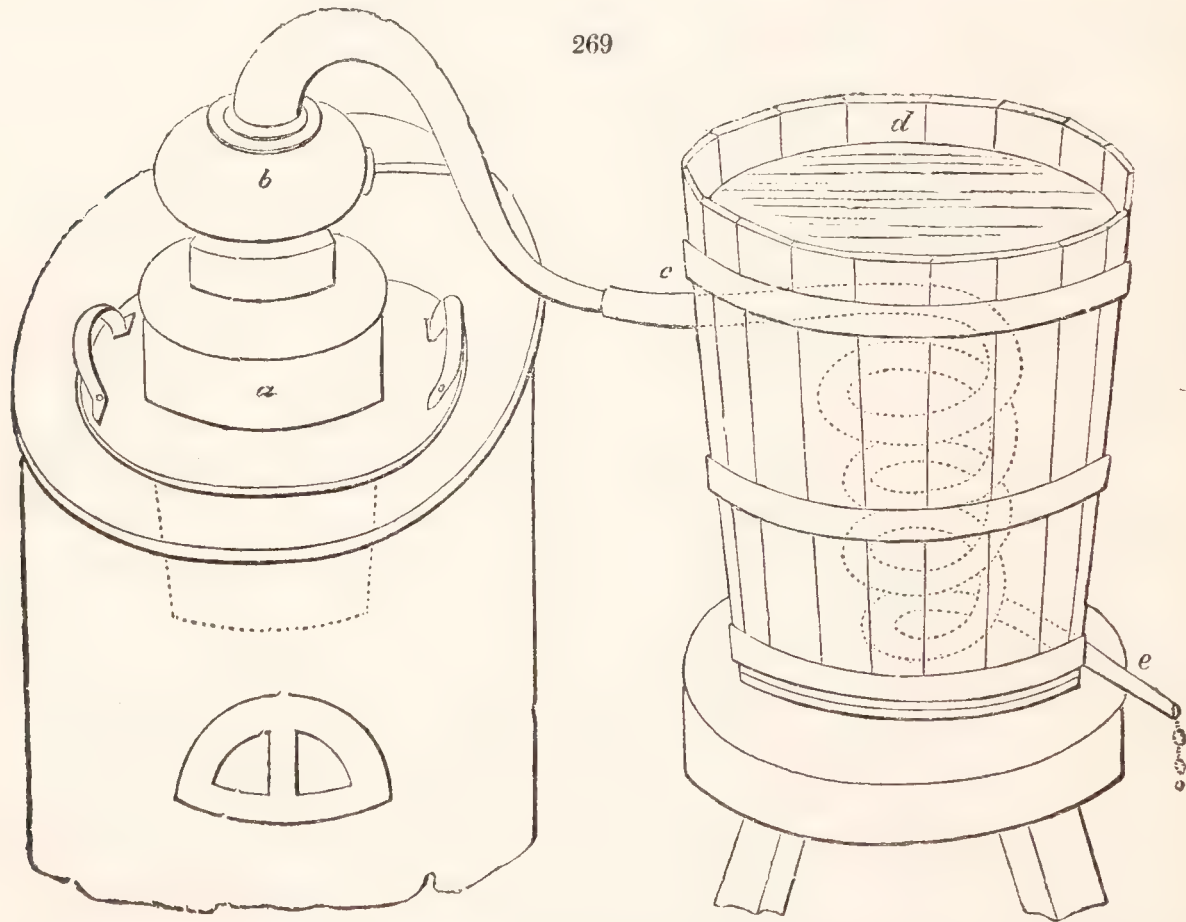
These river waters hold also variable quantities of suspended matters, dependent upon locality, state of weather, &c., so that the above represent the contents of the filtered waters.

The water from the shallow wells of London usually abounds in sulphate of lime, and often in carbonate of lime, containing generally but little chloride of sodium; the solid contents of the gallon are very variable, but sometimes reach 130 to 140 grains. The water is very hard, and yields in some cases considerable traces of oxide of manganese. The deep wells, which penetrate the London clay, and are carried to different depths into the underlying chalk, vary in the quality of their water according to the care with which the superincumbent springs have been excluded: they contain a larger relative proportion of solid matter than river water, but less than that found in the surface wells, and are remarkably characterised by the abundance of soda-salts, and by their alkalinity derived from carbonate of soda: like all the other waters, they hold more or less carbonic acid. The following are analyses of four of these Artesian springs:—1, is from Messrs. Combe and Delafield's brewery, near Long Acre (GRAHAM); 2, from the well of the Fountains in Trafalgar square (PLAYFAIR); 3, from the well of the Royal Mint: this well is 426 feet deep; namely, 226 feet of iron cylinder through the gravel, blue clay, plastic clay, and sands, and 200 feet bored into the chalk. The water rises in it to within 85 feet of the surface; it affords by the pumps at present at work 240 gallons of water per minute, by which the surface level is lowered in the course of the day about 25

feet, where it remains stationary, and when the pumping ceases, rapidly re-ascends to the original level; 4, is water from a deep well at Notting Hill.

	(1)	(2)	(3)	(4)
Carbonate of soda	11·68	14·56	12·20	12·2
Sulphate of soda	24·24	19·60	17·93	19·7
Chloride of sodium	12·75	25·72	9·33	19·1
Carbonate of lime	6·19	3·10	} 4·54.....	{ 5·7
Carbonate of magnesia	1·09	2·40		
Phosphate of lime	0·19	} 3·56		{ traces
Phosphate of iron	0·24			
Silica	0·44			
<hr/>				
Total solid matter in the } imperial gallon	56·82 grs.	68·94 grs.	44·00	60·6

The impurities of water are separated by *distillation*, which process is usually conducted upon the large scale in a copper *boiler*, *a*, placed either in a portable furnace (fig. 269,) or set in brickwork, according to its dimensions, to which is annexed the *still-head*, *b*, of the same mate-



rial, or of pewter, connected with the pewter *worm*, *c*, which is immersed in the *worm-tub*, or *refrigerator*, *d*, its lower end passing out at *e*. The water in this vessel must always be retained of a low temperature, to effect the condensation of the vapor in the spiral tube.

Distilled water, as commonly prepared, always affords minute traces of foreign matter, especially when subjected to Voltaic decomposition, and can only be considered as *perfectly* pure when re-distilled at a low temperature in silver vessels.

Pure water is transparent, and without either color, taste, or smell. It is a powerful refractor of light, and a very imperfect conductor of heat (p. 55) and of electricity (p. 216 *note*, and p. 237). In consequence of the facility of obtaining it pure, it is assumed as a standard to which the relative weights of all other solids and liquids may be compared, its specific gravity being called = 1·000; and hence the importance of estimating its

weight with precision (p. 41). At the temperature of 62° , which is that to which specific gravities are usually referred, a cubic inch of water weighs 252.458 grains; or at 60° , the cubic inch weighs almost exactly 252.5 grains, and the cubic foot 998.217 ounces *avoirdupois*, which is so near 1000, that the specific gravity of any substance, in reference to water, is very nearly the absolute weight of one cubic foot of such substance in *avoirdupois* ounces. The specific gravity of gold, for instance, is 19.3, in reference to water as unity, and, therefore, a cubic foot of gold weighs *nearly* 19,300 ounces. Water is about 815 times heavier than atmospheric air. Water at mean temperature is also assumed as the unit to which the specific heats of bodies (p. 61), especially of solids and liquids, are usually referred: the specific heat of water has been ascertained with much precision by Regnault. (*Ann. Ch. et Ph.*, LXXiii. 35.)

Water is susceptible of compression, as was originally shown by Canton. Perkins states that a pressure of 2000 atmospheres occasions a diminution of 1-12th its bulk. (*Phil. Trans.*, 1820.) This subject has been more recently examined into by Ørsted, whose results differ from those of Perkins: the estimate of the latter he thinks too great. (*Edin. Jour. Science*, xii., 201.) According to his experiments, and those of Colladon and Sturm, (*Ann. Ch. et Ph.*, xxxvi. 140,) its absolute diminution of bulk for each atmosphere is 51.3-millionths of its volume. It is stated by Dessaignes, that when water is submitted to very sudden compression, it becomes luminous. (THENARD, *Traité de Chimie*, i. 432.)

At the temperature of 32° water congeals into ice, which, if slowly formed, produces needles crossing each other at angles of 60° and 120° . Their forms are various, but the primitive figure has not been ascertained, though it is probably rhomboidal. The specific heat of ice is, according to Desains, about half that of water. (*Ann. Ch. et Ph.*, July, 1845.) The specific gravity of ice is 0.927 (OSANN), 0.950 (ROYER and DUMAS), 0.916 (BERZELIUS), the densest ice, obtained by freezing water deprived of air, being always considerably lighter than water. According to Brunner, the contraction of ice by diminution of temperature exceeds that of any other solid: its density at 32° being 0.918, at 18° it is 0.919, and at 0° , 0.920. (*Ann. Ch. et Ph.*, July, 1845.) Ice is a non-conductor, or nearly so, of electricity, and under favorable circumstances becomes electric by friction. (FARADAY'S *Exp. Researches*, 4th Series, § 381 and 419.) It is a very bad conductor of heat. In freezing, water expands with such force as to burst very thick and strong vessels in which it is confined. The rupture of iron and leaden pipes is a familiar instance of this power. The most interesting experiments upon the subject are those of Major Williams. (*Edin. Phil. Trans.*, vol. ii.) Bomb-shells, about 13 inches in diameter, and more than 2 inches thick, were filled with water; the fuse-holes were then plugged with iron-bolts, and, thus charged, were exposed to the open air at a temperature between -4° and -19° . At the moment of congelation the plugs were thrown out, and the ice protruded through the fuse-hole. When the plug was duly secured, the shell itself burst. The greatest difference observed in these experiments between the bulk of water before and after congelation was: 174 : 184. Exposed to the air, ice loses considerably in weight by evaporation. Hail is always crystallized in the form of two six-sided pyramids, applied

base to base; the faces of the two pyramids meet at angles of about 80° , and one of the pyramids is always truncated. (SMITHSON, *Ann. of Phil.*, 2nd series, v. 340.)

If water be exposed to heat in open vessels it boils, or is converted into steam, at 212° , the barometer being at 30 inches; but the boiling-point of water varies considerably with the pressure (p. 173,) and is singularly influenced by the air which it contains, and by other causes affecting its adhesion to the vessel in which it is heated, (DONNY, *Ann. Ch. et Ph.*, Fevrier, 1846): 100 cubical inches weighing, at the temperature of 212° , and under mean pressure, 14.96 grains, or at 60° , 19.3409 grains.

In the constitution of aqueous vapor or steam, *two* volumes of hydrogen and *one* of oxygen are condensed into *two* volumes, as in the annexed diagram. The specific gravity, therefore, of steam compared with that of hydrogen, is as 9 to 1: or 0.624 in reference to air as = 1, for

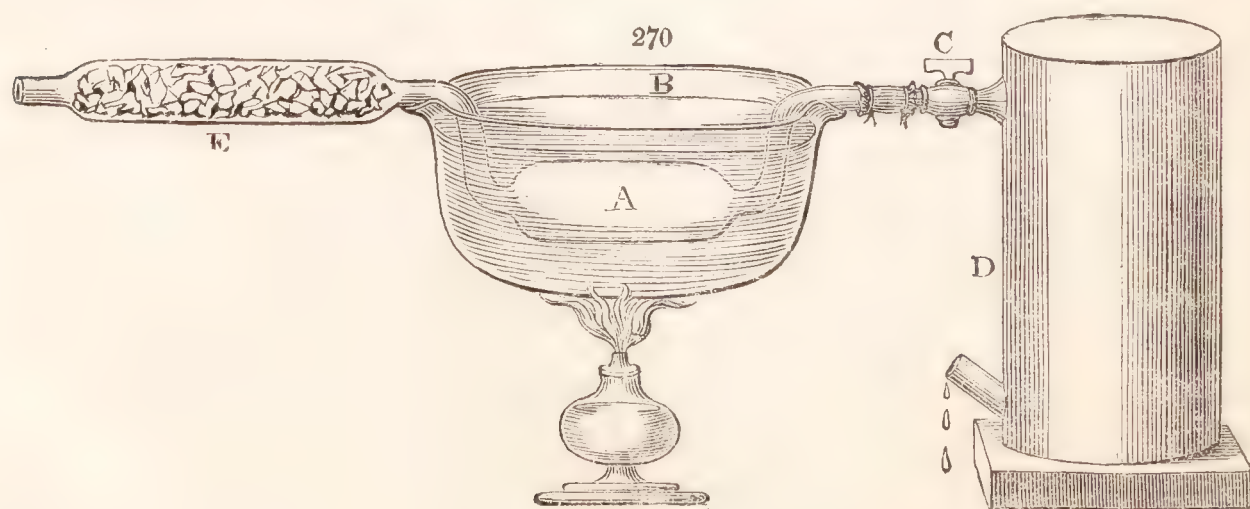
Hydrogen.	Oxygen.		Steam.
1	8	=	9

1 volume of hydrogen,	specific gravity	0.0693
$\frac{1}{8}$ „ oxygen	„	0.5546

Specific gravity of steam therefore = 0.6239

At mean pressure, and at the temperature of 212° , the bulk of steam is 1689 times that of water. (p. 71.)

Water enters into combination with a variety of substances, and is retained with various degrees of force: where it contributes to the regular form and transparency of crystallized bodies, it is termed *water of crystallization* (p. 6). In other cases the compounds which water forms with substances are called *hydrates*, as with many of the metallic oxides: in both cases it may be considered as one of the constituents of the bodies, for it exists in them in a definite proportion. But water is often only mechanically retained by substances, which are then said to be *hygrometric*, and the proportion of such water will vary with the texture of the substance, and the humidity of the atmosphere to which it has been exposed: it is often necessary to deprive substances of their hygrometric moisture, which may in many instances be done by simple exposure to a sufficient heat; but where the substance is easily decomposed, the heat must be kept below 212° , or in some cases, desiccation must be performed at lower temperatures, in which case the following arrangement may be employed:



The substance to be dried is introduced into the glass cylinder A, which may be made of any convenient diameter and length, and immersed in the water-bath B; it is connected at one end with the stop-cock c of the gas-holder D, which is filled with water, and its lower aperture left open, so that as the water flows out, it draws in air through the vessel A and the tube E, which latter is filled with pieces of fused chloride of calcium, so that the air may be thoroughly dried before it passes over the contents of the vessel A.

Water, which has been exposed to the atmosphere, always contains a portion of air, as may be proved by boiling it, or by exposing it under the exhausted receiver of the air-pump. To separate the air, the water must be continuously boiled in vacuo, for it is very obstinately retained. (DONNY, *Ann. Ch. et Ph.*, Fev. 1846.) It absorbs oxygen gas in preference to atmospheric air or nitrogen, and, when the air is expelled by boiling, the last portions contain more oxygen than those first given off. (HUMBOLDT and GAY LUSSAC, *Journal de Physique*, 1805.) It is by the oxygen thus dissolved in water that the blood of fishes is aërated, and as at great altitudes the quantity of the air in water is very small, in consequence of diminished pressure, it is found that fishes never thrive in alpine lakes.

Mr. Dalton states, that 100 cubical inches of spring water afford about two inches of air, which, after losing from 5 to 10 per cent. of carbonic acid by the action of lime-water, consists of 38 per cent. oxygen and 62 nitrogen. (*New System*, 271.) Dr. Henry obtained 4·76 cubic inches of gas from 100 of the water of a deep spring, of which 3·38 were carbonic acid gas, and 1·38 air, of the same standard as that of the atmosphere. There can, however, be no doubt, that the aëriform contents of different springs vary both in quantity and quality.

The following Table exhibits the quantity of different gases which water is capable of absorbing at mean temperature and pressure, the water being previously deprived of air by long boiling.

GASES.	100 Volumes of Water absorb		AUTHORITY.
Oxygen	3·7 volumes	Dalton.
Chlorine.....	200	Gay Lussac.
Oxide of chlorine	800	Stadion.
Hydrogen	1·56	Henry.
Hydrochloric acid.....	50000 average	Davy.
Hydriodic acid			
Nitrogen	1·56	Henry.
Nitrous oxide	100	Ditto.
Nitric oxide	5		
Nitrous acid			
Ammonia	67000 average		
Sulphurous acid.....	3000	Davy.
Sulphuretted hydrogen.....	100	Dalton.
Phosphuretted hydrogen	2·14	Henry.
Do.....	12	Davy.
Carbonic oxide	2 average		
Carbonic acid.....	100	Dalton.
Carburetted hydrogen	12·5	Dalton.
Cyanogen	450	Gay Lussac.
Fluoboric acid	70000	John Davy.
Fluosilicic acid	35000	Saussure.
Hydroselenic acid.....	300	Berzelius.

The great importance of water as a natural and artificial agent, both mechanical and chemical, must be sufficiently obvious. The manner in which its changes of state or form influence the temperature of the globe, will be evident by a reference to the details given in the section on heat. When it freezes, the expansion which it suffers, and the force with which its particles arrange themselves in the crystalline form, are often actively concerned in the disintegration and decay of rocks and strata, and in the production of soils. Water is a most general and useful solvent, especially of saline bodies, the relative solubilities of which will be stated under their individual chemical history. It is also an important vehicle of other more fixed substances in the form of vapor: there are many saline substances, fixed in themselves, but of which minute portions rise along with the vapor of water during the ebullition of their solutions, and the volatile oils, many of which have boiling points greatly above that of water, readily pass over in large quantities, when associated with steam. It has been assumed by some that plants may possibly derive portions of their fixed ingredients from atmospheric sources; but although some fixed salts no doubt are carried up in small quantities when their solutions are boiled, it by no means follows that they should also thus rise along with the vapor of water generated at much lower temperatures. Considered as a chemical agent, water is frequently resolved into its elements; these are sometimes respectively concerned in the production of new compounds: when chloride of phosphorus, for instance, acts upon water, its chlorine combines with the hydrogen to form hydrochloric acid, and the phosphorus and oxygen unite to form phosphorous acid. In other cases bodies decompose water by the absorption of oxygen only, and the hydrogen is liberated; but there is no instance in which the hydrogen is absorbed, and the oxygen evolved.

PEROXIDE OF HYDROGEN. OXYGENATED WATER. HO_2 or $\text{H}\ddot{\text{O}}$. This singular compound was discovered by Thenard, in 1818: he obtained it by dissolving the *peroxide of barium* in hydrochloric acid and water, and adding sulphuric acid, by which the *protoxide* of barium is precipitated in the state of sulphate, and the excess of oxygen transferred to the water: by several repetitions of this process the water is gradually saturated with oxygen. There are so many difficulties attending the whole process, that it has been seldom repeated, and we know little of the nature of this extraordinary compound, except through the original essays of its discoverer: it has been surmised, from its properties, and mode of formation, that it may be an aqueous solution of liquid oxygen; Thenard, however, regards it as a definite combination of hydrogen and oxygen, in which one atom of the former is combined with two of the latter, as follows:—

					Thenard.	Volumes.
Hydrogen.....	1	1	5.9 6.02
Oxygen	2	16	94.1 93.98
<hr/>						
Peroxide of Hydrogen .	1		17		100.0	100.00

Much of the success of the process for obtaining this compound depends upon the purity of the peroxide of barium: the following details are from Thenard's memoir. (*Ann. Ch. et Ph.*, viii. ix. x. and L.; THENARD'S *Traité de Chim.*, Ed. 4, ii., p. 41.)

To obtain pure peroxide of barium, prepare a pure nitrate of baryta, and give it a strong heat in a porcelain vessel, by which, baryta, not quite pure, but containing traces of silica and alumina but no manganese, will be obtained; the latter impurity must always be most cautiously avoided, for oxide of manganese possesses the property of energetically decomposing the oxygenated water. The baryta, broken into small pieces, is then introduced into a luted glass tube (the glass should not contain lead) large enough to contain about two pounds of it, and being heated to dull redness, a current of dry and perfectly pure oxygen gas is passed through it, which it rapidly absorbs; this operation is to be continued till the oxygen escapes from a small tube inserted into the opposite extremity of the larger one. The *peroxide of barium* thus obtained is pale gray, and frequently some pieces are speckled with green, which announces the presence of manganese, and which should be rejected: its distinctive character is, that it crumbles when a few drops of water are added to it, without producing heat.

The process then proceeds as follows. Take a certain quantity of water, (about eight ounces for instance,) and add to it a sufficiency of pure and fuming hydrochloric acid to dissolve about 230 grains of baryta: put this acid liquor into a glass vessel, which, during the operation, must be surrounded by ice: then take about 185 grains of the peroxide, rub it into a fine paste with a little water in an agate mortar, and put it into the acid liquor with a box-wood spatula: it soon dissolves without effervescence: to this solution add pure sulphuric acid, drop by drop, stirring it with a glass rod, till it is in slight excess, which is known by the readiness with which the sulphate of baryta falls: then dissolve a second portion of the peroxide and precipitate as before, taking care to use enough, but not too much, sulphuric acid. The liquor is now to be filtered, and the residue washed with a little water, so as to keep up the original measure by adding it to the first portion: a second and third washing of the residue with very small quantities of water may be advisable, and these liquors should be kept apart for the purpose of washing the filters in subsequent operations.

A fresh portion of the peroxide is then dissolved in the filtrated liquor and decomposed as before, filtering at every two operations, and washing the filter with the savings of the others; we thus proceed till the water is sufficiently oxygenated. When about two pounds of the peroxide have been consumed, the water will be united to about thirty times its volume of oxygen, which is as much as it will retain, unless some hydrochloric acid be added, in which case M. Thenard has made it retain 125 volumes.

When the water is sufficiently oxygenated, it is retained in the ice, and supersaturated with the peroxide of barium, which occasions the separation of floeculi of silica and alumina, colored with a little oxide of iron and of manganese; the whole is then filtered as quickly as possible, and returned into the vessel surrounded by ice; the baryta is separated by sulphuric acid; and pure sulphate of silver is added, to separate the hydrochloric acid, upon which the liquid, before milky, becomes suddenly clear. The sulphuric acid is ultimately separated by baryta, the liquor filtered, and placed in a shallow vessel, under the air-pump receiver, including a basin of sulphuric acid; the receiver being

exhausted, the water evaporates and is absorbed by the acid, while the *peroxide of hydrogen*, being less vaporisable, remains: if it give out any oxygen, which sometimes happens, from its containing impurities, a drop or two of weak sulphuric acid will prevent its further evolution.

The peroxide of hydrogen thus concentrated has the following properties: its specific gravity is 1.45; it is colorless and inodorous; it blisters the cuticle of the tongue, and has a peculiar metallic taste. It does not congeal when exposed to cold, unless diluted. It is rapidly decomposed at a heat below 212° , and very slowly at ordinary temperatures; it may be long kept at 32° . It is decomposed by the voltaic pile with the same phenomena as water. (?) It is decomposed by all metals except iron, tin, antimony, and tellurium: the metals should be finely divided, or in powder: silver and oxide of silver decompose it very suddenly with the evolution of heat and light: platinum and gold produce the same phenomena; lead and mercury slowly separate the oxygen. Orpiment and powdered sulphuret of molybdenum act upon it with the same violence as silver; the peroxides of manganese and of lead also occasion its instant decomposition.

SUBOXIDE OF HYDROGEN. H_2O . Paul succeeded in condensing 1 volume of hydrogen into 3 volumes of water; and De Marty states that water gradually combines with hydrogen, taking up in the course of two years nearly its own volume. Gmelin therefore (*Handbuch*, i. 533,) infers the existence of a suboxide, which, according to Kästner (*Berliner Jahrbuch*, 1820), is also formed by repeatedly saturating cooled water with sulphuretted hydrogen, and abstracting the sulphur by proper metals.

HYDROGEN AND CHLORINE. HYDROCHLORIC ACID. MURIATIC ACID. CHLORHYDRIC ACID*. HCl . When equal volumes of hydrogen and chlorine are mixed, and exposed to light, they slowly combine, and produce *hydrochloric acid gas*. If the mixture be exposed to the direct solar rays, detonation often ensues, as was first remarked by Gay Lussac and Thenard. (*Recherches Physico-Chimiques*, ii. 129.) It also frequently detonates when suddenly exposed to the intense light of the voltaic discharge passing between charcoal points, and if the experiment be made in a tube over water, a peculiar vibratory motion of the surface of the water in the tube is generally observed, previous to the explosion. That direct solar light is not necessary to effect this combination has been shown by Professor Silliman, (*American Journal of Science*, iii. 342; *Ann. Phil.*, xix. 153,) who relates a case of the explosion of the mixed gases in dull and cloudy daylight. This fact furnishes a caution against mixing any considerable quantities of chlorine and

* This is a *hydrogen-acid*, or *hydracid*, of which there are several; some with simple, others with compound bases; iodine, bromine, and fluorine, form with hydrogen acids analogous to the hydrochloric, and these constitute an important and well-defined group; sulphur, selenium, arsenic, tellurium, phosphorus, and a few other substances, form a second group; and a third includes the hydracids with compound bases, such as the hydrocyanic, &c. The hydracids do not com-

bine with basic oxides to produce salts, but when they act on such oxides, a mutual decomposition of the oxide and of the acid ensues: thus when soda (oxide of sodium) is added to hydrochloric acid, the sodium of the base and the chlorine of the acid unite to form chloride of sodium, and the oxygen of the base and the hydrogen of the acid form water. So also when hydrocyanic acid and oxide of silver react upon each other, water and cyanide of silver are the results.

hydrogen. The agency of light on these gases may be beautifully shown by filling a tube, about half an inch in diameter, and twelve inches long, with the mixed gases, and alternately shading it with an opaque cover, and exposing it to the sun's rays. The moment the tube is exposed even to the diffused light of day, a cloudiness appears within it, and the water ascends more or less rapidly, according to the intensity of the light. The effect even of a passing cloud is distinctly seen in retarding the rapidity of the combination, which is very striking in the full solar light. (HENRY, *Elements*, vol. i.) Seebeck states that the mixed gases, exposed to the sun's rays in a tube of violet-colored glass, combine rapidly, but without explosion, and that in a tube of red glass they scarcely act upon each other. Under the perfect exclusion of light the gases do not combine. According to Döbereiner, a mixture of 1 volume of hydrogen with 1.5 chlorine explodes more readily than equal volumes. Draper's *actinometer* is founded upon this action of radiant matter.

The best mode of showing the composition of hydrochloric acid, is to introduce into a small but strong glass vessel a mixture of equal volumes of the two gases, and to inflame them by the electric spark; no change of volume ensues, and hydrochloric gas results: the apparatus shown at fig. 230 may be used for this purpose. Or a jet of hydrogen may be inflamed and introduced into a jar of chlorine; during its combustion the yellow color of the chlorine disappears, and hydrochloric acid is formed. The mixed gases do not explode under the influence of spongy platinum, at common temperature.

Sir H. Davy found that the heat evolved during the combustion of a mixture of equal volumes of chlorine and hydrogen exceeded that produced by a mixture of oxygen and hydrogen, and that the former mixture was inflamed at a lower temperature, and would bear much greater rarefaction than the latter, without losing its explosive property. Oxygen and hydrogen ceased to explode when rarefied 18 times, but chlorine and hydrogen retain their combustibility when rarefied 24 times.

By passing a succession of electric sparks through hydrochloric acid gas Dr. Henry effected its partial decomposition, and when it had gone to a certain extent, the gases again combined: he also found, that by passing a mixture of oxygen and hydrochloric acid gas through a red-hot porcelain tube, or by the transmission of electric sparks, water was formed and chlorine evolved. At the temperature of 250° , the same change was produced upon the mixture by spongy platinum. (*Phil. Trans.*, 1812 and 1824.)

Hydrochloric acid gas may also be decomposed by the action of several of the metals. (DAVY, *Phil. Trans.*, 1810.) Potassium, for instance, absorbs the chlorine, and the hydrogen is evolved. This experiment is best made by introducing a piece of potassium into a small retort, which is then to be exhausted and filled with hydrochloric acid gas from a jar standing over mercury. The potassium generally takes fire, but is sometimes prevented burning by the formation of a film of chloride of potassium, and then requires to be heated, which, however, should be done carefully, as the retort is apt to break in consequence of the intensity of the combustion that ensues; an accident, however, which may be prevented by placing the potassium in a small platinum capsule. When it has cooled it will be found that the residuary gas is *hydrogen*, equal to

half the original bulk of the hydrochloric acid. If a piece of burning potassium be introduced in a small copper spoon into a bottle filled with hydrochloric acid gas, the metal continues in vivid combustion, and the evolved hydrogen at the same time takes fire, and sometimes burns at the neck of the bottle. Tin and lead heated in the gas also effect its de-

composition, and evolve exactly half its bulk of hydrogen. The greater number of metallic oxides when heated in gaseous hydrochloric acid, decom-

Hydrogen.	Chlorine.		Hydrochloric Acid.
1	36	=	37

pose it; metallic *chlorides* are formed, and the oxygen of the oxide combining with the hydrogen of the acid forms water.

The specific gravity of hydrogen to chlorine is as 1 to 36; and one volume of hydrogen and one of chlorine combine to form two volumes of hydrochloric acid gas, as shown in the above diagram; or (according to Davy, and to Gay Lussac and Thenard), hydrochloric acid gas consists of

					Volumes.	Sp. Gr.
Hydrogen	1	1	2·7 1
Chlorine.....	1	36	97·3 1
Hydrochloric acid	1		37		100·0	2

This gas was discovered by Priestley in 1772: it is generally procured by acting upon common salt, or sal-ammoniac, by sulphuric acid; it must be received over mercury. The salt should be put in fragments into a small tubulated retort, which may be one-fourth filled with it: the sulphuric acid should barely cover the pieces of salt; the gas is instantly extricated, and when its evolution slackens, it may be quickened by the gentle heat of a lamp. It is convenient to put a long strip of folded blotting-paper into the neck of the retort, which absorbs any liquid that may chance to go over, and prevents its soiling the mercury. With a little practical dexterity, clean and dry bottles may be conveniently filled with this gas by displacement as described at page 269.

As the specific gravity of hydrochloric acid gas compared with air is 1·262; and as it consists of equal volumes of hydrogen and chlorine combined without change of volume, 100 cubical inches must weigh 39·36 grains; for

50	cubic inches of hydrogen	weigh	1·069
50	„ chlorine	„	38·299
100	„ hydrochloric acid gas	„	39·368

According to Thomson, 100 cubic inches at 32° weigh 42·126 grains.

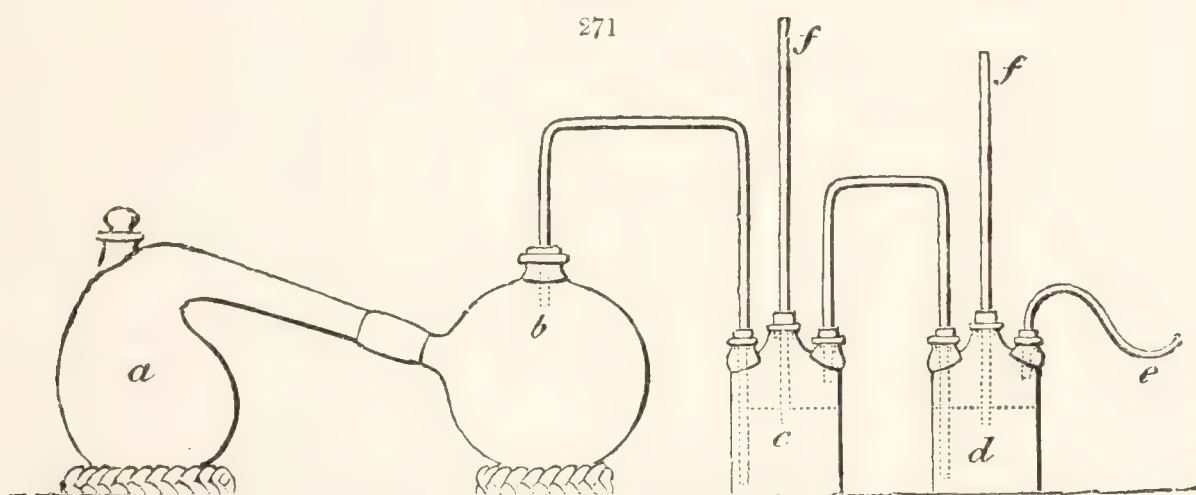
Although permanently gaseous at all common temperatures and pressures, Mr. Faraday liquified this gas by generating it in a sealed tube, so as to expose it to a pressure of about 40 atmospheres at 50°. It was colorless, and possessed a refractive power inferior to that of water. He could not succeed in solidifying it. (*Phil. Trans.*, 1823; and 1845, p. 163.)

Hydrochloric acid gas is perfectly unrespirable; it extinguishes the flame of a taper, and is itself unflammable. It irritates the skin. It has a strong attraction for water; and when it escapes into the air it forms visible fumes, arising from its combination with aerial vapor. A piece of ice let up into the gas over mercury, immediately liquifies and absorbs

it: and if a tall jar of the gas be carefully transferred, with its mouth downwards, from the mercurial to the water-trough, the water instantly rushes in with violence, and fills it. Litmus-paper is powerfully reddened by this gas, and turmeric-paper receives from it a brown discoloration not unlike the effect of an alkali.

Water takes up 480 or 500 times its bulk of hydrochloric acid gas, and has its specific gravity increased from 1 to 1.210. (H. DAVY.) This may be shown by throwing up a few drops of water into a tall jar of the gas standing over mercury; the gas disappears, and the mercury fills the vessel. There is considerable elevation of temperature during this condensation of the gas.

For saturating any quantity of water with gases which are easily soluble in that fluid, we generally employ *Woulfe's apparatus*, one form of which is shown in the annexed cut. *a* is a tubulated retort, in which



the materials producing the gas or vapor are contained; *b*, a receiver communicating by a bent tube with the three-necked bottle *c*, which is connected also by a tube with *d*. These bottles are about half-filled with water, or other fluid intended to be saturated with the gas; when that in *c* has become saturated, it passes into *d*, and afterwards through the tube *e*, which may be so arranged as to convey away the superfluous gas. In case absorption should take place in the vessels *a* or *b*, the pressure of the external air might force the water from *d* into *c*, and from *c* into the balloon *b*. This is prevented by the safety-tubes *ff*, which, dipping not more than half an inch under the surface of the water, allow a little air to enter, so as to compensate for the absorption. The different joints may be secured either by grinding, or by well-cut corks rendered tight by a mixture of drying-oil and pipe-clay.

When gaseous hydrochloric acid is thus dissolved in water, it forms the *liquid hydrochloric acid*, commonly called *muriatic acid* or *spirit of salt*, which was discovered by Glauber about the middle of the seventeenth century. It is generally procured by distilling a mixture of dilute sulphuric acid and common salt. The proportions directed in the *London Pharmacopœia* are two pounds of salt and 20 ounces of sulphuric acid, diluted with 12 ounces of water. The retort containing these ingredients may be luted on to a receiver, containing the same quantity of water used in diluting the sulphuric acid, and the distillation carried on in a sand-bath. The specific gravity of the product is stated to be 1.160, and 100 grains of it should be saturated by 132 grains of crystallized carbonate of soda. The quantity of real acid in

hydrochloric acid of different densities is best ascertained by the quantity of pure carbonate of lime (Carrara marble, for instance), which a given weight of the acid dissolves. Every 50 grains of the carbonate are equivalent to 37 of real acid.

In preparing this acid upon the large scale an apparatus of earthenware is sometimes used, similar to that described under the article *Nitric Acid*; the market, however, might easily be supplied with hydrochloric acid to any amount, were the demands adequate; for in the operations in which common salt is decomposed for the manufacture of carbonate of soda, enormous quantities of hydrochloric acid are evolved, and often allowed to pass into the chimney.

When this acid is pure, it is colorless, but it generally has a yellow hue arising from particles of cork or lute that have accidentally fallen into it, or sometimes from a little iron. Dr. Thomson suggests that the pale yellow tint occasionally observed in this acid apparently pure, may possibly arise from a trace of bromine, derived from the salt. The acid of commerce almost always contains iron and sulphuric acid, and sometimes nitric and sulphurous acid. The iron may be detected by the black tint produced by tincture of galls, in the acid previously diluted and saturated by carbonate of soda. If a solution of chloride of barium, dropped into the diluted acid, occasion a white cloud or precipitate, it announces sulphuric acid. The presence of nitric acid (and of free chlorine and bromine?) is shown by boiling some gold-leaf in the suspected hydrochloric acid, and then dropping into it a solution of protochloride of tin, which, if nitric acid were present, produces a purplish tint, showing the gold to have been acted upon, which it is not by pure hydrochloric acid. Sulphurous acid is indicated by the addition of a few crystals of protochloride of tin, which, after standing, produces a brown precipitate, containing sulphur in combination with tin. (GIRARDIN.) The presence of sulphurous acid is also indicated by adding a little solution of chloride of barium, filtering off any sulphate of baryta that may be thrown down, and then boiling with a little nitric acid, which occasions a fresh precipitation of sulphate of baryta. (GMELIN.) Free chlorine in the acid discolors solution of indigo. Saline substances may be detected by evaporating the acid to dryness: when pure, it leaves no residue. Traces of arsenic may also exist in hydrochloric acid derived from the sulphuric acid used in its formation. (See ARSENIC.)

The highly-concentrated liquid acid (sp. gr. 1.20) emits copious fumes when exposed to air, and boils, according to Dalton, at a temperature of about 112°*: it freezes at -60°. When mixed with water, it occasions a slight elevation of temperature. It is decomposed by many substances

* The variation of the boiling-point with the density of hydrochloric acid is shown in the following table by Dalton, from which it appears that it is highest when it contains between 19 and 20 per cent. of the gas: the strong acid becoming weaker, and the weak acid stronger by boiling.

Sp. Gr.	Boil. pt.	Sp. Gr.	Boil. pt.	Sp. Gr.	Boil. pt.
1.166	170°	1.121	228°	1.035	219°
1.154	190	1.094	232	1.018	216
1.144	212	1.075	228	1.009	214
1.136	217	1.064	225		
1.127	222	1.047	222		

containing loosely-combined oxygen, such as chloric, iodic, and bromic acids, and several of the metallic peroxides. Its decomposition by peroxide of manganese, for the production of gaseous chlorine, has already been referred to: in this case, oxygen is imparted by the oxide to the hydrogen of the acid, so as to form water, and the chlorine previously in combination with the hydrogen is liberated; at the same time a chloride of manganese is formed. In this case, 1 atom of peroxide of manganese, and 2 atoms of hydrochloric acid, give rise to the production of 2 atoms of water and 1 atom of chloride of manganese, 1 atom of chlorine being evolved. The elements which are employed are

1 atom Manganese.....	= 28	2 atoms Hydrogen	= 2
2 atoms Oxygen.....	= 16	2 „ Chlorine	= 72
<hr/>			
1 atom Peroxide of } Manganese	} = 44	2 „ Hydrochloric } acid	} = 74
<hr/>			

The products of their mutual reaction are

1 atom Manganese.....	= 28	2 atoms Hydrogen.....	= 2
1 „ Chlorine.....	= 36	2 „ Oxygen.....	= 16
<hr/>		<hr/>	
1 „ Chloride of } Manganese	} = 64	2 „ Water	= 18
<hr/>			
1 atom Chlorine = 36.			

or, in symbols, $\text{MnO}_2, 2\text{HCl} = \text{MnCl}, 2\text{HO}, \text{Cl}$.

The decomposition of hydrochloric by nitric acid will be afterwards explained.

When metallic zinc is put into strong liquid hydrochloric acid it is rapidly decomposed, and the *hydrogen* copiously evolved may be burned as it escapes; some peroxide of lead added to another portion of the acid immediately disengages *chlorine*, which may be shown by its bleaching power upon a piece of paper dipped into indigo blue: this experiment well illustrates the separation of the two elements of the acid. In the voltaic circuit its chlorine is evolved at the positive electrode or anode, and its hydrogen at the negative electrode or cathode, so that when thus electrolysed and tinged with indigo, a bleaching effect is produced at the anode (p. 222).

Uncombined hydrochloric acid exists in small quantity in the human gastric juice; it is not found in nature except as an occasional volcanic product. The principal uses of this acid are as a medicine, and in some of the arts, where it is chiefly employed as a solvent of metals. It has been used in the gaseous state as a disinfectant, but is more annoying, and less efficient than chlorine; indeed, by some, its disinfecting powers have been altogether denied. It is extremely injurious to vegetation: mixed with 20,000 times its volume of atmospheric air, it proves fatal to plants, shrivelling and killing all the leaves in twenty-four hours. (CHRISTISON and TURNER.)

The following tables by Mr. E. Davy and by Dr. Thomson show the value and atomic composition of hydrochloric acid of different densities; Dr. Ure, in his *Dictionary*, has also published an extended table upon the same subject; the data upon which it is formed and several important facts connected with this subject, will be found in his paper relating to it in the *Quarterly Journal of Science* (xii. 286).

(Temp. 40° Fah., Bar. 30.)

Specific Gravity.	100 Grains contain of Hydrochloric Gas.	Atoms of Water to 1 of Acid.	Real Acid in 100 of the Liquid.	Specific Gravity.
1·21	42·43			
1·20	40·80	6	40·66	1·203
1·19	38·38	7	37·00	1·179
1·18	36·36	8	33·95	1·162
1·17	34·34	9	31·35	1·149
1·16	32·32	10	29·13	1·139
1·15	30·30	11	27·21	1·128
1·14	28·28	12	25·52	1·119
1·13	26·26	13	24·03	1·112
1·12	24·24	14	22·70	1·106
1·11	22·30	15	21·51	1·100
1·10	20·20	16	20·44	1·096
1·09	18·18	17	19·47	1·090
1·08	16·16	18	18·59	1·086
1·07	14·14	19	17·79	1·082
1·06	12·12	20	17·05	1·078
1·05	10·10			
1·04	8·08			
1·03	6·06			
1·02	4·04			
1·01	2·02			

It appears from Dr. Thomson's table that the strongest liquid hydrochloric acid contains 1 atom of real acid + 6 atoms of water; when this is evaporated

in the air, acid escapes, and it comes, according to Graham, to contain 1 atom of acid + 12 of water. According to Dr. Clark, the acid which is unaltered by distillation contains about 16 atoms of water: the density of the vapor of this acid is 0·691, so that it consists of 1 volume of hydrochloric gas, combined without change of bulk with 8 volumes of steam. (BINEAU, *Ann. Ch. et Ph.*, LXVIII. 422.)

HYDROGEN AND IODINE. HYDRIODIC ACID. HI. This compound of hydrogen and iodine was first examined by Davy and Gay Lussac. (*Phil. Trans.*, 1814. *Ann. de Ch.*, xci.) Hydriodic acid may be formed by the direct union of its elements, as by passing a mixture of hydrogen and the vapor of iodine through a red-hot tube. It cannot be obtained by the action of sulphuric acid upon iodide of sodium or potassium, because the hydriodic and sulphuric acids partially decompose each other, evolving iodine, and forming sulphurous acid and water. It is most easily procured by the mutual action of water, phosphorus, and iodine; or, what amounts to the same thing, by the action of iodide of phosphorus on water. In thus procuring it, it is convenient to use a tube retort, into the bulb of which is introduced the moist iodine, and a small stick of phosphorus, about a tenth part of the weight of the iodine, placed in the neck above it, which can be shaken down upon the iodine when the beak of the tube or retort is placed under the inverted jar; a quantity of the gas is instantly generated, and a further portion is obtained on applying the flame of a spirit-lamp. In this case decomposition of the water and of the iodide ensue, and phosphorous and hydriodic acids are the results. Upon the same principle it may be obtained by previously preparing iodide of phosphorus, and gently heating it with a little water; if too high a temperature be used, phosphuretted hydrogen is also given off.

Millon recommends gently heating a mixture of 1 part of phosphorus, 14 of iodide of potassium, 20 of iodine, and a little water: the formula of the action is $2\text{KI} + 5\text{I} + \text{P} + 7\text{HO} = 2\text{KO}, \text{PO}_5 + 7\text{HI}$. (GMELIN.)

According to D'Arcet, hydriodic acid gas may be obtained very pure by the following process: Hydrophosphorous acid is to be evaporated until upon the point of evolving phosphuretted hydrogen gas. It is then to be put, with its weight of iodine, into a small tube retort; the gas is liberated, upon applying a gentle heat: 100 grains of the acid, and 100 of iodine, afforded 120 cubical inches. The residue of the operation is a mixture of phosphoric acid and of the compound of hydriodic acid and phosphuretted hydrogen. (*Ann. Ch. et Ph.*, xxxvii. 220.)

Whichever process is followed, if the gas be received over mercury it should be transferred as fast as possible into an exhausted vessel, as it is otherwise soon decomposed. It may often be conveniently collected by displacement, in dry phials, without a mercurial trough, as in the method described at p. 269.

Hydriodic acid gas is colorless, sour, exhales fumes in the air, and smells like hydrochloric acid. It strongly reddens vegetable blues. Its specific gravity compared with air is as 4.4024 to 1; 4.3757 (THOMSON), 4.4429 (GAY LUSSAC); 100 cubic inches weigh about 136 grains (or 142.4 grains at the temperature of 32° . THOMSON.) Compared with hydrogen, its specific gravity is as 63.5 to 1. It extinguishes flame, and is not itself inflammable. It is liquifiable under pressure, (KEMP, *Phil. Mag. & Jour.*, vii. 444,) and becomes a transparent colorless solid at about -60° ; at a point a little higher it becomes a clear liquid, and this point is close upon that which corresponds to a vaporous pressure of one atmosphere; at 0° , its pressure was = 2.9, at 32° = 3.97, and at 60° = about 5.86 atmospheres. (FARADAY. *Phil. Trans.*, 1845, p. 161.) It is not permanent at a red heat, for when passed through a red-hot porcelain tube it is partially resolved into iodine and hydrogen.

Hydriodic gas is rapidly and abundantly absorbed by water, but in what exact proportion has not been determined. The saturated solution, exposed to a temperature below 260° , becomes concentrated by loss of water; at about 260° it boils, and may be distilled. The specific gravity of the strongest liquid acid is 1.7. It becomes dark-colored when kept in contact with air, in consequence of a partial decomposition. It is decomposed by chlorine and by nitric and sulphuric acid.

The *aqueous hydriodic acid* is best prepared by passing sulphuretted hydrogen through a mixture of iodine and water: sulphur is deposited, and on heating and filtering the liquor a pure solution of hydriodic acid is obtained, which may be concentrated by evaporation. It may also be obtained by heating iodine, phosphorus, and water; or by passing sulphuretted hydrogen through a solution of 1 part of iodine in 16 of alcohol, filtering, diluting with 32 of water, and subsequent distillation to drive off the alcohol and excess of sulphuretted hydrogen.

When hydriodic acid gas is mixed with oxygen, and passed through a red-hot tube, it is resolved into iodine and water. Its decomposition by chlorine produces hydrochloric acid, sometimes with explosion, and the blue vapor of iodine is rendered evident, but presently disappears in consequence of the formation of chloride of iodine. This decom-

position is beautifully shown by suffering hydriodic acid gas to pass into a jar of atmospheric air, mixed with about a twelfth its bulk of chlorine; the violet fumes are then more permanent. A little strong nitric acid dropped into hydriodic acid gas energetically decomposes it, with the evolution of so much heat that the gas is occasionally inflamed. (TURNER.)

The experiments of Gay Lussac have proved the composition of hydriodic acid gas to be analogous to that of the hydrochloric: namely, that it consists of 1 volume of the vapor of iodine, and 1 of hydrogen; these produce 2 volumes of the acid. By the action, for instance, of mercury and some other metals, hydriodic acid gas is decomposed, the iodine being absorbed by the metal, and evolving from 2 volumes of the gas, 1 of hydrogen: so that

Hydrogen.	Iodine.	=	Hydriodic Acid.
1	126		127

the annexed diagram represents its composition. That such is the composition of this acid is also shown by its weight, for,

			Grs.
50	cubic inches of hydrogen weigh	1.06
50	„ „ iodine vapor	134.92
100	„ „ hydriodic gas	135.98

Or, it consists of

						Volumes.	Sp. Gr.
Hydrogen	1	1	0.8 1 0.069
Iodine	1	126	99.2 1 8.735
Hydriodic acid	1		127		100.0 2 4.402

Hydriodic acid dissolves iodine; so likewise do the solutions of iodide of potassium and of zinc, taking up a quantity of iodine equal to that which they already contain: these compounds have been termed *ioduretted iodides*, and are by some considered as containing a peculiar acid which may be termed *hydriodous acid*, composed of 1 atom of hydrogen = 1 + 2 of iodine = 126 × 2 = 252. (BAUP, *Journ. de Pharm.*, ix. p. 40.)

The hydriodic acid is not found uncombined in nature: some of its combinations have already been mentioned under the head of *iodine*. Its presence may be detected by mixing a cold solution of starch with the liquid suspected to contain it, and then adding a few drops of a solution of chlorine or of nitric or sulphuric acid: this liberates iodine, and produces a blue tint.

HYDROGEN AND BROMINE. HYDROBROMIC ACID. HBr. Bromine and hydrogen do not act upon each other, even under the influence of the sun's rays, at common temperatures; but when bromine, phosphorus, and water, are brought into contact, a decomposition ensues, analogous to that described under the article *hydriodic acid*, and *hydrobromic gas* is generated, which may be collected over mercury, or in dry phials. It is also evolved on gently heating a mixture of 1 part of phosphorus, 12.5 of bromine, and 7.8 of bromide of potassium, with a little water. (MILLON.) Hydrobromic acid may be formed by acting upon a mixture of bromine

vapor and hydrogen by a coil of red-hot platinum wire; and it is evolved when bromide of potassium is decomposed by sulphuric acid, but in this case a portion of it is apt to be decomposed.

This compound, though gaseous at common temperatures and pressures, condenses into a clear colorless liquid at 100° below 0° : at 124° below 0° it is a transparent crystalline solid: it does not freeze until reduced much lower than this temperature, but, being frozen by the carbonic acid bath in vacuo, it remains a solid until the temperature attains -120° . (FARADAY. *Phil. Trans.*, 1845, p. 161.)

Hydrobromic acid gas is colorless, sour, of a pungent and highly irritating odor, and yields dense vapors when mixed with humid air. It undergoes no change when passed through a red-hot tube, either alone or mixed with oxygen or iodine; but chlorine decomposes it, producing vapor and drops of bromine, which, being absorbed by mercury, leaves hydrochloric acid. We learn, therefore, that the attraction of bromine for hydrogen exceeds that of iodine, but is inferior to that of chlorine. The attraction of oxygen, and of bromine for hydrogen, is probably nearly equal; for bromine does not decompose water, nor does oxygen decompose hydrobromic acid. Hydrobromic gas is not altered by mercury, but tin and potassium entirely decompose it; the former requires the aid of heat; but potassium acts at common temperatures, diminishing the gas to half its bulk, and forming bromide of potassium. Hence it appears that the constitution of hydrobromic acid is analogous to that of hydrochloric and hydriodic acids, and that it consists of equal volumes of hydrogen and bromine vapor. The

Hydrogen.	Bromine.		Hydrobromic Acid.
1	78	=	79

weight therefore of 100 cubic inches of hydrobromic acid will be as follows:

	Grs.
50 cubic inches of hydrogen weigh	1.06
50 " " bromine vapor	84.00
<hr/>	<hr/>
100 " " hydrobromic gas	85.06

Or, it consists of

					Volumes.	Sp. Gr.
Hydrogen.....	1	1	1.266 1 0.069
Bromine	1	78	98.734 1 5.400
<hr/>	<hr/>		<hr/>		<hr/>	<hr/>
Hydrobromic acid	1		79		100.000	2 2.734

Hydrobromic acid gas is rapidly absorbed by water: heat is evolved, and a fuming liquid acid obtained, which is colorless when pure, but which readily dissolves bromine, and acquires a yellow color. The specific gravity of the densest aqueous hydrobromic acid is 1.29. (LÖWIG.) It boils below 212° , losing hydrobromic gas, and having its boiling-point consequently elevated. This aqueous acid may also be obtained by the action of sulphuretted hydrogen on bromine and water. It is instantly decomposed and discolored by chlorine. Nitric acid also decomposes it, evolving bromine, and forming water and nitrous acid. This mixture dissolves gold and platinum. Hydrobromic acid is not readily decomposed

by sulphuric acid; but on decomposing bromide of potassium by sulphuric acid, a little sulphurous acid is generally formed.

HYDROGEN and FLUORINE—HYDROFLUORIC ACID. HF. This acid was made known by Scheele: the process for procuring it pure was first suggested by Knight. (*Phil. Mag.*, xvii. 357.) Its properties were examined by Gay Lussac and Thenard in 1810, (*Recherches Physico-chimiques*,) and by Davy. (*Phil. Trans.* 1809-1813.) When finely-powdered *fluoride of calcium*, or *fluor spar*, as it is usually called, (carefully selected for its purity and freedom from silica,) is distilled with twice its weight of sulphuric acid, a highly volatile and corrosive liquid, which is *hydrofluoric acid*, is obtained: $\text{CaF}_2 + \text{SO}_3\text{H}_2 = \text{CaO}\cdot\text{SO}_3 + \text{HF}$. It acts powerfully on glass and on most of the metals: the retort employed in the experiment may be of lead, with a tube and receiver of platinum; the receiver must be immersed in a mixture of ice and salt. The product is best preserved in a platinum bottle, with a well-fitted stopper of the same metal. When pure, it is clear, colorless, very volatile, and smokes when exposed to air: at temperatures above 60° it flies off in vapor. Its specific gravity is 1.0609; but by the gradual addition of a certain proportion of water it acquires a considerable increase of density, the mixture having a specific gravity of 1.25. Its attraction for water exceeds that of oil of vitriol; and when dropped into water it excites a hissing noise, and great heat is evolved. Its vapor is dangerously pungent and irritating, and the liquid acid is eminently active upon organic substances; a minute drop of it upon the skin produces a painful sore, and in larger quantities dangerous and malignant ulceration: hence the vessels containing it require to be handled with great caution. Its most characteristic property is the energy with which it acts upon glass: its vapors soon destroy the polish and transparency of all neighbouring glass vessels, and when dropped upon glass, great heat and effervescence are produced, and dense fumes evolved, consisting of *fluosilicic acid*. Diluted with about six parts of water, the acid may be used for *etching upon glass*, which it effectually accomplishes in a few minutes.

The nature of this powerful and peculiar acid is as yet imperfectly understood, its basis, *fluorine*, not having been obtained in an insulated form. All analogy, however, leads us to regard it as a compound of fluorine and hydrogen. In the voltaic circuit hydrogen is evolved from it at the negative electrode, and the positive platinum wire corroded and converted into a brown compound, probably of fluorine and platinum. Many of the metals also decompose it with the evolution of hydrogen; and peculiar compounds result, *fluorides*, consisting of the metal in combination with fluorine. The action of potassium upon this acid is very energetic; it is attended by explosion, by the liberation of hydrogen, and by the formation of a peculiar soluble saline compound which is considered as a *fluoride of potassium*. Kuhlman's experiments are also quite consistent with these views: he found that pure fluor spar (fluoride of calcium) was not in the least acted upon, even at a red-heat, by anhydrous sulphuric acid; and that when hydrochloric acid was transmitted over fluor spar at a red-heat hydrofluoric acid was disengaged and chloride of calcium formed. It cannot therefore be doubted that hydrofluoric

acid, as originally suggested by Davy, is analogous to the other hydracids (*Phil. Trans.*, 1813, p. 263):

that it may therefore be regarded as composed of equal volumes of hydrogen and fluorine combined, without

condensation, its atomic constitution being

Hydrogen.	Fluorine.		Hydrofluoric Acid.
1	19	=	20

Hydrogen	1	1	5	Berzelius.
Fluorine	1	19	95	5·05
Hydrofluoric acid	1		20		100		94·95
							100·00

§ VII. NITROGEN. N. 14.

NITROGEN, or *Azote*, was first recognised as a distinct aëriform fluid by Dr. Rutherford in 1772. (Thesis, *De Aëre Mephitico*.) Dr. Priestley called it *phlogisticated air*.

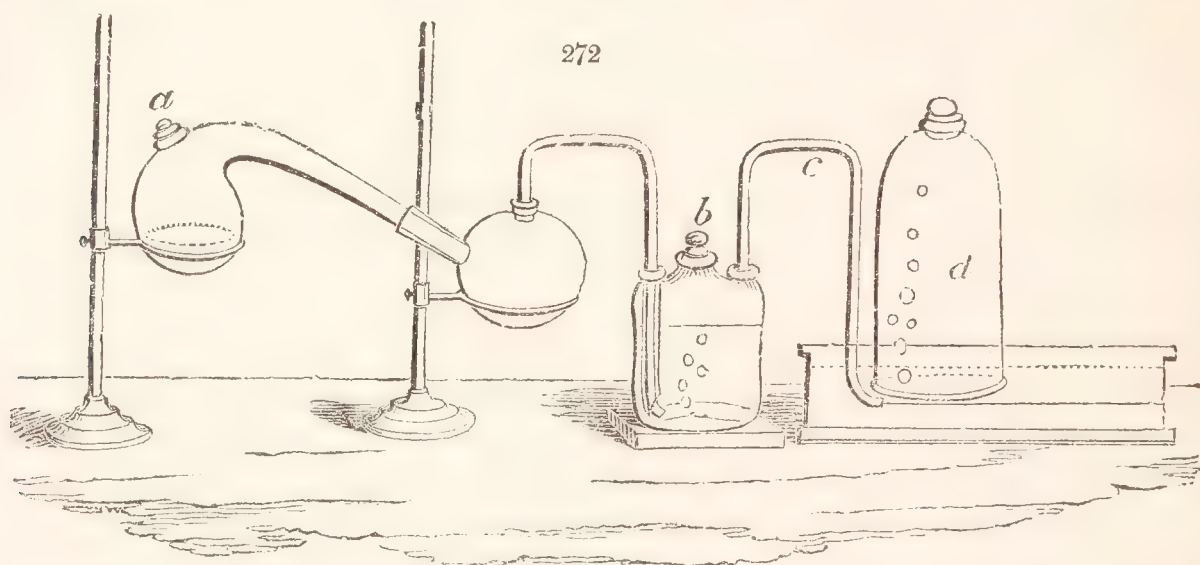
Nitrogen may be obtained by burning phosphorus in a confined portion of atmospheric air. For this purpose a tall glass jar should be selected, open at bottom, and stopped at the top: a small porcelain or metallic cup, containing a sufficiency of inflamed phosphorus, is then set afloat in the water-trough, and the jar, without its stopper, immediately inverted over it. A quantity of air is at first expelled by the heat: the stopper is then replaced, and the combustion goes on for some time; when it has ceased, and the apparatus has cooled, the cup is easily removed by agitating the jar, so as to sink it through the water; the residuary gas is then thoroughly washed with lime water, and is nitrogen nearly pure.

According to Berzelius, the purest nitrogen is obtained by filling a bottle about one-third full of a liquid amalgam of lead and mercury, carefully stopping it, and agitating it with the included air for two hours or more; the highly-divided lead absorbs the oxygen, and leaves pure nitrogen. On opening the bottle under water, the liquid rushes in, and demonstrates the degree of absorption.

If equal weights of iron-filings and sulphur be made into a paste with water, and exposed in a confined portion of atmospheric air, it will, in the course of forty-eight hours, absorb the oxygen, and leave the nitrogen nearly pure. Dumas and Boussingault obtained pure nitrogen by passing air previously deprived of moisture by sulphuric acid, and of carbonic acid by potassa, over finely-divided metallic copper at a red heat.

Another mode of obtaining nitrogen, which furnishes it in a state of considerable purity, consists in passing chlorine into a strong aqueous solution of ammonia. This may be done by nearly filling a Wolfe's bottle with two necks with the solution, and passing gaseous chlorine into it from a retort containing hydrochloric acid and oxide of manganese; a bent tube issuing from the other neck passes under the shelf of the pneumatic apparatus, and through it the nitrogen escapes, and may be collected; but care should be taken to leave excess of ammonia in the bottle, lest explosive chloride of nitrogen should be formed. In this experiment ammonia, consisting of hydrogen and nitrogen (see AMMONIA), is decomposed by the chlorine, which unites with its hydrogen to form hydrochloric acid, and gaseous nitrogen is evolved: a solution of

hydrochlorate of ammonia is at the same time obtained, and if excess of chlorine be used, chloride of nitrogen, a dangerously explosive compound, may be formed. If the ammoniacal solution be very concentrated, the bubbles of chlorine often produce flashes of light and slight explosions: these are harmless, and may be prevented by dilution of the ammonia. The following is the disposition of the apparatus: *a* is the retort and tubulated receiver containing the materials for the evolution of chlorine; *b* the two-necked bottle about three-fourths filled with strong liquid ammonia; *c* a bent tube, carrying the evolved nitrogen into the water-trough, where it is collected in the inverted jar *d*.



There are other processes by which nitrogen may be obtained, some of which will be noticed under the article *Atmospheric Air*. It is also frequently evolved during the decomposition of animal matter. If lean muscular flesh, for instance, be heated in nitric acid diluted with ten or twelve parts of water, this gas is given off, though not pure: these cases of its evolution will be more particularly explained afterwards.

Nitrogen is a permanently elastic colorless gas, with neither smell nor taste, having no action upon vegetable colors or upon lime-water; neither is it absorbed by water, except that fluid has been deprived of its ordinary portion of air by long boiling, when it takes up about one and a half *per cent*. Its refractive power in regard to light is to that of atmospheric air as 1.0340 to 1.0000. It is rather lighter than atmospheric air, compared with which its specific gravity is 0.971: 100 cubic inches weigh at mean temperature and pressure 30.15 grains. At 32° the weight of 100 cubic inches is 31.879 grains. (THOMSON.) Its specific gravity in reference to hydrogen is as 14 to 1.

An animal immersed in nitrogen is suffocated, whence it was called by Lavoisier *azote* (from *a*, privative, and ζωή, life): but if that term be taken in its strict sense, all gaseous bodies (excepting atmospheric air) might be included under it; for even oxygen itself will not indefinitely support life: moreover, nitrogen, as it exists in the atmosphere, mixed with oxygen, appears to be absolutely essential to animal life; for no other gas can be substituted for it. Its influence in *respiration*, as a component of atmospheric air, will be considered afterwards. It is contained in many organic bodies. If we consider the term *nitrogen* as merely implying that it is a component of nitric acid, it is explicit and unobjectionable.

The electro-chemical relations of nitrogen are still obscure, and

whether it is or is not an ion has not been determined. How far it deserves to be called an *inflammable substance* is not obvious: its attraction for oxygen is not powerful, and the two bodies when mixed in their gaseous state show no tendency to combine; they do, however, unite in several proportions, but their compounds are mostly formed at low temperatures, or the nitrogen and oxygen are presented to each other in their *nascent states*, that is, before one or both of them have acquired the independent gaseous form. The same remark applies to all compounds of this gas.

Nitrogen is, in the strictest sense of the word, a non-supporter of combustion; for all burning bodies are immediately and perfectly extinguished by it: this is the case with the flame of a taper, with phosphorus in intense combustion, and even with potassium, which, however highly heated, shows no inclination to burn in pure nitrogen.

Under certain circumstances, however, nitrogen may be made to undergo a kind of combustion, as when electric sparks are passed through atmospheric air, or through a mixture of one volume of nitrogen with two or three of oxygen: in this case each spark will be attended by the production of a trace of nitric acid, and after some hundred sparks, the blue of litmus will be changed to red (p. 236). Here combustion appears to take place in that portion of the gas immediately subject to the action of the sparks; but the temperature of the surrounding gas is not thus sufficiently elevated to enable the combustion to spread beyond the immediate sparks. Berzelius has well compared this action to that which ensues when sparks are passed through a mixture of hydrogen and a large relative quantity of atmospheric air or of oxygen; in that case no general combustion of the mixture is effected; but water is slowly formed by the action of each successive spark upon the portion of the gaseous mixture immediately subjected to its heating influence; and it is probable that the electric spark made to act upon mixtures of nitrogen and oxygen under considerable pressure might be more effective in inducing combination; but few of the nitric compounds are stable, or capable of sustaining a continued red-heat without decomposition.

If a mixture of nitrogen with twelve or fourteen volumes of hydrogen be set fire to as it issues from a small tube, and burned either in common air or in oxygen, water and nitric acid will be formed; so that in this case the nitrogen may be said to undergo combustion by the aid of the elevated temperature of the flame of hydrogen; but it must be recollected that in these cases nitric acid could not be produced without the presence of water, and that it may tend to dispose an union which would not otherwise take place. The formation of a trace of nitric acid when hydrogen is burned in common air is referable to the same cause.

Much discussion has arisen respecting the nature of nitrogen; and the question has been agitated, whether it is or is not a *simple body*; but although many ingenious surmises have been published on the subject, and many analogies suggested in favor of its compound nature, no experimental proofs have been hitherto adduced: Sir H. Davy (*Elements of Chem. Philos.*, 474) and Berzelius have each discussed this question, chiefly in reference to the phenomena of the supposed *metallisation of ammonia* (see MERCURY); and the latter has proposed the name *nitricum* for the imaginary base of nitrogen, assuming that gas to be a suboxide.

(*Lehrbuch*, i. 208.) He has also adverted to the supposed formation of nitrogen by graminivorous animals, but this question will more properly be considered when upon animal products.

NITROGEN AND OXYGEN. These bodies unite in *five proportions*, and form the following compounds:

1. Nitrous oxide	-	-	-	NO
2. Nitric oxide	-	-	-	NO ₂
3. Hyponitrous acid	-	-	-	NO ₃
4. Nitrous acid	-	-	-	NO ₄
5. Nitric acid	-	-	-	NO ₅

PROTOXIDE OF NITROGEN, NITROUS OXIDE, NO, or $\dot{\text{N}}$, was discovered by Priestley, in 1776; he called it *dephlogisticated nitrous air*: it has also been called *gaseous oxide of azote*. It may be formed by exposing *nitric oxide* (NO₂) to the action of iron-filings, or of a mixture of sulphur and iron-filings, by which one equivalent of its oxygen is absorbed, and the remaining elements left in such proportions as to constitute nitrous oxide. But the gas thus procured is not pure. It is most easily and abundantly obtained in a state of purity by heating *nitrate of ammonia* in a glass retort over an Argand lamp, to a temperature of about 420°. The gas which passes off, provided the salt be pure, and the temperature not too high, may be collected over warm water, and is pure *nitrous oxide*. $\text{NH}_4\text{O}, \text{NO}_5 = 2\text{NO}, 4\text{HO}$. If the nitrate of ammonia contain a mixture of the hydrochlorate, the gas will be contaminated by chlorine; and if too much heat be used in the decomposition of the pure salt (which may be known by white vapors appearing in the retort) it will contain nitric oxide. The salt should be kept in a state of gentle ebullition, so as to maintain a quick but not violent evolution of gas.

The presence of *chlorine* in nitrous oxide is ascertained by its smell, and may be avoided by using pure nitrate of ammonia, the solution of which should not be rendered turbid by nitrate of silver. *Nitric oxide* is detected in it by the appearance of red fumes on mixing the gas with oxygen: it may be abstracted by agitating it with a solution of *protosulphate of iron*, which has no action upon nitrous oxide, but absorbs the nitric oxide, and acquires a deep olive color. If nitrous oxide be mixed with *oxygen* or with *common air*, it affords red fumes upon adding to it a few bubbles of nitric oxide, and it is not, as it ought to be, entirely absorbed when agitated with thrice its bulk of cold water.

100 cubic inches of nitrous oxide weigh 47·220 grains; its specific gravity, therefore, to hydrogen, is as 22 to 1; and to atmospheric air as 1·5252 to 1000. At the temperature of 32°, 100 cubic inches weigh 49·978 grains. (THOMSON.) Its taste is slightly sweet, and its odor peculiar, but agreeable. It is absorbed when agitated with water, which takes up about its own bulk, and evolves it unchanged when heated; it should, therefore, be collected and preserved in stopped bottles. It is also absorbed by alcohol and ether, and by fixed and volatile oils.

Nitrous oxide was generally considered not only as unrespirable, but as eminently noxious; the attempts, however, that had been made to breathe it, were with an impure gas: when obtained perfectly pure, Sir H. Davy found that it might be breathed when mixed with common air,

without any injurious effects, and he afterwards ventured upon its respiration in a pure state, and discovered its singular effects upon the system, which in many respects resemble those of intoxication. (*Researches Chemical and Philosophical, chiefly concerning Nitrous Oxide.* London, 1800.) The experiment of breathing this gas, however, cannot be made with impunity, especially by those who are liable to a determination of blood to the head. The following accounts will serve to give a general idea of its singular powers. They are quoted from Sir H. Davy's *Researches*, in which many important details concerning the effects of different gaseous bodies upon the system will be found. The first account is by Mr. Tobin, and the second by Dr. Roget:—

“On the 29th of April I breathed four quarts from and into a silk bag. The pleasant feelings produced at first, urged me to continue the inspiration with great eagerness. These feelings, however, went off towards the end of the experiment, and no other effects followed. The gas had probably been breathed too long, as it would not support flame. I then proposed to Mr. Davy, to inhale the air by the mouth from one bag, and to expire it from the nose into another. This method was pursued with less than three quarts, but the effects were so powerful as to oblige me to take in a little common air occasionally. I soon found my nervous system agitated by the highest sensations of pleasure, which are difficult of description; my muscular powers were very much increased, and I went on breathing with great vehemence, not from a difficulty of inspiration, but from an eager avidity for more air. When the bags were exhausted and taken from me, I continued breathing with the same violence; then suddenly starting from the chair, and vociferating with pleasure, I made towards those that were present, as I wished they should participate in my feelings. I struck gently at Mr. Davy; and a stranger entering the room at the moment, I made towards him, and gave him several blows, but more in the spirit of good humour than of anger. I then ran through different rooms in the house, and at last returned to the laboratory somewhat more composed; my spirits continued much elevated for some hours after the experiment, and I felt no consequent depression either in the evening or the day following, but slept as soundly as usual.”

Dr. Roget states as follows:—“The effect of the first inspirations of the nitrous oxide was that of making me vertiginous, and producing a tingling sensation in my hands and feet; as these feelings increased, I seemed to lose the sense of my own weight, and imagined I was sinking into the ground. I then felt a drowsiness gradually steal upon me, and a disinclination to motion: even the actions of inspiring and expiring were not performed without effort; and it also required some attention of mind to keep my nostrils closed with my fingers. I was gradually roused from this torpor by a kind of delirium, which came on so rapidly that the air-bag dropt from my hands. This sensation increased for about a minute after I had ceased to breathe, to a much greater degree than before, and I suddenly lost sight of all the objects around me, they being apparently obscured by clouds, in which were many luminous points, similar to what is often experienced on rising suddenly and stretching out the arms, after sitting long in one position. I felt myself totally incapable of speaking, and for some time lost all consciousness of

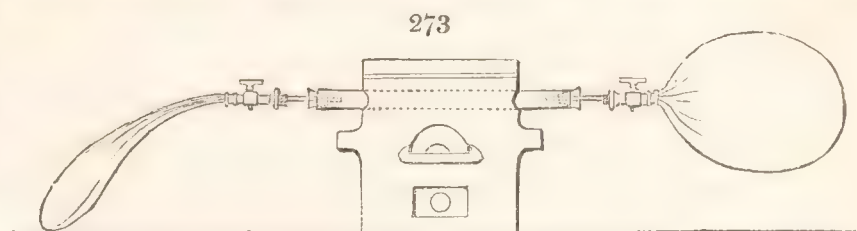
where I was, or who was near me. My whole frame felt as if violently agitated: I thought I panted violently; my heart seemed to palpitate, and every artery to throb with violence; I felt a singing in my ears; all the vital motions seemed to be irresistibly hurried on, as if their equilibrium had been destroyed, and everything was running headlong into confusion. My ideas succeeded one another with extreme rapidity, thoughts rushed like a torrent through my mind, as if their velocity had been suddenly accelerated by the bursting of a barrier which had before retained them in their natural and equable course. This state of extreme hurry, agitation, and tumult, was but transient. Every unnatural sensation gradually subsided; and in about a quarter of an hour after I had ceased to breathe the gas, I was nearly in the same state in which I had been at the commencement of the experiment. I cannot remember that I experienced the least pleasure from any of these sensations. I can, however, easily conceive, that by frequent repetition I might reconcile myself to them, and possibly even receive pleasure from the same sensations which were then unpleasant. I am sensible that the account I have been able to give of my feelings is very imperfect. For, however calculated their violence and novelty were to leave a lasting impression on the memory, these circumstances were for that very reason unfavorable to accuracy of comparison with sensations already familiar. The nature of the sensations themselves, which bore greater resemblance to a half-delirious dream than to any distinct state of mind capable of being accurately remembered, contributes very much to increase the difficulty, and as it is above two months since I made the experiment, many of the minuter circumstances have probably escaped me."

Nitrous oxide is not permanently elastic; by subjecting it to a pressure of about 50 atmospheres at the temperature of 45° , Faraday obtained it in the liquid form. It was thus procured by sealing up some nitrate of ammonia in a bent tube and heating it, while the other end was kept cool. Many explosions occurred with very strong tubes, and the experiment is always attended with risk. The tube, when cooled, is found to contain two fluids: the heavier is water, a little acid; the lighter, *liquid nitrous oxide*; it is limpid, colorless, and so volatile, that the heat of the hand generally makes it disappear in vapor. The application of ice and salt condenses it again. Its refractive power is less than that of any known fluid. (*Phil. Trans.*, 1823, p.195.) Natterer condensed nitrous oxide into the liquid state by the use of pumps only (*Comptes rendus, &c.*, Nov. 1844), and Faraday subsequently succeeded in solidifying it at a temperature of about 150° below 0° . (*Phil. Trans.*, 1845, p.176.)

Nitrous oxide supports combustion, and a taper introduced into it has its flame much augmented, and surrounded by a purplish halo. Phosphorus and sulphur, when introduced in a state of vivid ignition into this gas, are capable of decomposing it, and burn with the same appearance nearly as in oxygen; but if, when put into the gas, they are merely burning dimly, they then do not decompose it, and are extinguished; so that they may be melted in the gas, or even touched with a red-hot wire without inflaming. Charcoal, and many of the metals, also decompose nitrous oxide at high temperatures.

At a red-heat this gas is decomposed, and two volumes of it are resolved into two volumes of nitrogen and one volume of oxygen, so that

it thus suffers an increase of bulk. For experiments of this kind the following simple apparatus may be used; it consists of two bladders, one of which is filled with the gas, and the other empty, attached to the extremities of a coated porcelain or platinum tube, which traverses the body of a furnace. The bladders are supplied with stop-cocks, and the gas is pressed from one to the other when the tube is red-hot.



The analysis of this gas may also be effected by detonation with hydrogen. When a mixture of one volume of nitrous oxide and one volume of hydrogen is fired by the electric spark, water is produced, and one volume of nitrogen remains. Now, as one volume of hydrogen takes half a volume of oxygen to form water, nitrous oxide must consist of two volumes of nitrogen and one volume of oxygen; these three volumes being so condensed, in consequence of chemical union, as only to fill the space of two volumes. The specific gravity of nitrogen, compared with oxygen, is as 14 to 16; the composition, therefore, of the nitrous oxide, may be represented as annexed: and as

Nitrogen.	Oxygen.		Nitrous Oxide.
14	8	=	22

	Grains.
100 cubic inches of nitrogen weigh	30·166
50 " oxygen	17·054
100 " nitrous oxide	47·220

Hence, regarding this gas as a *protoxide*, the atomic weight of nitrogen will be 14, or, according to Dr. Turner and Berzelius, 14·25; (*Phil. Trans.*, 1833;) but the more recent experiments of Dumas have established the accuracy of 14 (upon the hydrogen scale, consistently with the original determination of Prout,) and nitrous oxide will be constituted as follows:—

					Davy.	Volumes.	S. G.
Nitrogen	1	14	63·6	63·3	1·0	0·97	
Oxygen	1	8	36·4	36·7	0·5	0·55	
<hr/>							
Nitrous oxide	1	22	100·0	100·0	1·0	1·52	

DEUTOXIDE OF NITROGEN. BINOXIDE OF NITROGEN. NITRIC OXIDE.

NITROUS GAS. NO_2 or $\ddot{\text{N}}$, was first procured by Mayow, but its properties were first accurately studied by Priestley. It is usually obtained by presenting certain substances to *nitric acid*, which abstract a portion of its oxygen, leaving the remaining elements in such proportions as to constitute the gas in question; for this purpose some copper-filings or clippings may be put into a gas-bottle with nitric acid diluted with thrice its bulk of water; an action ensues, red fumes are produced, and there is a copious evolution of the gas, which may be collected and preserved over water. In this mode of obtaining the gas 3 atoms of copper and 4 of nitric acid produce 3 of nitrate of copper and 1 of nitric oxide.

$4\text{NO}_5 + 3\text{Cu} = 3[\text{CuO}, \text{NO}_5] + \text{NO}_2$. The first portions should be rejected, as containing nitrogen and nitrous acid gas. Nitric oxide is presently recognised by the red fumes which it produces when brought into the contact of air; and if pure it is entirely absorbed by an aqueous solution of protosulphate of iron.

Nitric oxide is a colorless, uncondensable gas; its specific gravity to hydrogen is as 15 to 1. 100 cubic inches weigh 32.13 grains; and, compared with air, its specific gravity is as 1.0399 to 1000. According to Thomson, its specific gravity is 1.0416, and at the temperature of 32° 100 cubic inches weigh 34.1543 grains. Under common circumstances it is permanent over water; but if agitated with water previously deprived of air by long boiling, it is dissolved in the proportion of about 1 volume to 20. This solution, when long kept, is found to contain nitrate of ammonia, resulting from the joint decomposition of the nitric oxide and the water.

It is instantly fatal to animals; but as it will always meet with a sufficiency of oxygen in the lungs, to convert a part of it into nitrous acid, its abstract effects cannot be determined. An account of an attempt to breathe it will be found in Sir H. Davy's *Researches*, &c., p. 475. When it has been washed with water it is not acid, as may be proved by the color of litmus remaining unchanged by it. It extinguishes the flame of a taper, and that of sulphur, but phosphorus readily burns in it, if introduced in intense ignition, although it also is extinguished unless it be in vivid combustion. In this case the phosphorus decomposes the gas, nitrogen is evolved, and phosphoric acid formed. Charcoal also decomposes it at a high temperature, the results being carbonic acid and nitrogen.

Nitric oxide is not altered by a low red-heat, but it is decomposed when passed and repassed through small tubes heated to bright redness, more especially if the heated surface is increased by filling them with fragments of rock crystal, or by the introduction of platinum wire: it does not detonate when mixed with two volumes of hydrogen, and subjected to the electric spark; a succession of sparks, however, passed through such a mixture, slowly effects the decomposition of a portion of the gas; the same mixture is also decomposed by spongy platinum at common temperatures, and water and ammonia are formed, according to Dulong and Thenard, but Döbereiner denies this. When a mixture of 2 volumes of this oxide and 5 of hydrogen are passed by a small tube through the tubulature of a retort containing spongy platinum, and after the expulsion of the air, heated, the platinum becomes ignited, and water and ammonia are formed. $\text{NO}_2, 5\text{H} = \text{NH}_3, 2\text{HO}$. (HARE.) When this mixture with hydrogen is kindled in contact of air by a taper, it burns with a green flame, and water and nitrous acid are the results; so that the hydrogen only appears to be burned: an inflamed jet of hydrogen is extinguished in nitric oxide. Dr. Henry has shown that nitric oxide detonates with ammonia (*Phil. Trans.*, 1809,) in the proportion of 150 measures of the former to 100 of the latter. These gases also slowly act upon each other at common temperatures. Gay Lussac found that in about a month they were reduced to half their joint volume, and that nitrogen was evolved. Some substances which have a strong attraction for oxygen, effect a partial decomposition of the

nitric oxide, and convert it, at common temperatures, into nitrous oxide; such, for instance, as moist iron-filings, some of the alkaline sulphurets, some of the sulphites, and protochloride of tin; in which cases two volumes of nitric oxide afford one of nitrous oxide. Nitric oxide may also be decomposed by the action of some of the metals at high temperatures, which absorb its oxygen. Sir H. Davy decomposed it by heated arsenic, and by the ignition of charcoal. (*Elements*, 260.) Gay Lussac decomposed 100 measures of it by the action of heated potassium: 50 measures of pure nitrogen remained, and the loss of weight corresponded to 50 measures of oxygen; so that one volume of nitric oxide is thus resolved into equal volumes of oxygen and nitrogen. (*Mémoires d'Arcueil*.) Nitric oxide then is constituted of one volume of nitrogen and one volume of oxygen, combined as in the above diagram, without change of volume;

Nitrogen.	Oxygen.	=	Nitric Oxide.
14	8		

or 50 cubic inches of nitrogen, weighing			Grains.
and 50	„	oxygen	15·08
			17·05
form 100	„	nitric oxide	32·13

				Berzelius.	Vols.	Sp. Gr.
Nitrogen	1	14	46·67	46·754	1	0·9706
Oxygen	2	16	53·33	53·246	1	1·1093
Nitric oxide	1	30	100·00	100·000	2	1·0399

The most characteristic property of nitric oxide, by which it is immediately distinguished from all other gases, is that of forming the red fumes of hyponitrous or nitrous acid vapor when mixed with oxygen: hence these gases are mutually used to detect each other's presence; and as the nitrous acid is absorbed by water, oxygen may be abstracted from any gaseous mixture containing it in an uncombined state, by the addition of a sufficient quantity of nitric oxide; and, on the other hand, nitric oxide may be removed by the addition of oxygen. Priestley, who was the first to attempt accurate experiments upon this subject, conceived that the absorption was at all times uniform; but subsequent experiments have shown that it is subject to variation, more especially dependent upon the presence or absence of water. Although, therefore, nitric oxide may be used to ascertain the presence of oxygen, it cannot be relied on as an exact indicator of its proportional quantity; and although Dalton (*Ann. of Phil.*, x. 38,) and Gay Lussac (*Mém. d'Arcueil*, ii. 247,) have each proposed methods by which they conceive accuracy may be ensured, they are not such as to admit of general application. The best mode of using the nitric oxide to determine the proportion of oxygen to that of nitrogen in the atmosphere, will be noticed under the head of Atmospheric Air (EUDIOMETERS.)

Solutions of the protochloride and protosulphate of iron absorb nitric oxide gas; the color of these solutions is deep olive, and they speedily absorb oxygen when exposed to, or agitated with air, or other

mixtures containing it. (See EUDIOMETERS.) This property also enables us, as above stated, to ascertain the purity of nitric oxide, which ought to be wholly absorbed by the solution of iron: some nitrogen or nitrous oxide are thus generally detected in it, and remain unabsorbed. According to Peligot (*Ann. Ch. et Ph.*, liv. 17,) the proportion of nitric oxide absorbed by protosulphate of iron is definite, and in the ratio of 1 equivalent of the nitric oxide to 4 of the protoxide of iron; by exposure to a vacuum the nitric oxide escapes, and the salt of iron remains unaltered; but when heated, a part only of the nitric oxide is evolved, and part is decomposed, and peroxide of iron and ammonia are formed: when this solution is exposed to air or oxygen, nitric acid is ultimately produced.

When nitric oxide is perfectly dry, chlorine exerts no action upon it, but the presence of water causes an immediate change; it is decomposed, and, furnishing oxygen to the nitric oxide, and hydrogen to the chlorine, hyponitrous and hydrochloric acids are generated. It was the presence of water which misled those who thought that the red fumes produced by mixing nitric oxide and chlorine over water, resulted from the existence of oxygen in chlorine.

CHLORONITROUS GAS. According to E. Davy (*Phil. Mag.*, ix. 355,) when fused chloride of sodium is moistened with nitric acid, a pale reddish yellow gas is evolved, composed of equal volumes of chlorine and nitric oxide, combined without condensation.

HYPONITROUS ACID. AZOTOUS ACID. NITROUS ACID of Graham, Berzelius, and most foreign authors. NO_3 or $\ddot{\text{N}}$. Gay Lussac concluded, from his experiments, that there exists a compound of nitrogen and oxygen intermediate between nitric oxide and nitrous acid, to which the term *hyponitrous acid* may be applied. (*Ann. Ch. et Ph.*, i. 399.) He found by mixing nitric oxide and oxygen in tubes standing over mercury, and containing a little concentrated solution of potassa, that 400 volumes of nitric oxide were condensed under such circumstances by 100 of oxygen. When, however, he attempted to decompose the *hyponitrite of potassa* thus obtained, nitric oxide was evolved, and nitrous acid formed.

Dulong obtained hyponitrous acid (mixed with nitrous acid) by passing a mixture of 1 measure of oxygen with somewhat more than 4 of nitric oxide, first through a tube filled with fragments of porcelain to ensure perfect mixture, and afterwards through a bent tube, cooled below 0° ; the acid collected in the curvature was a dark-green fluid, more volatile than nitrous acid, and when distilled leaving a yellow fluid, which appeared to be nitrous acid. Liebig obtained hyponitrous acid by heating 1 part of starch in 8 of nitric acid, sp. gr. 1.25, and conducting the evolved gases first through a tube filled with fragments of chloride of calcium, and then into a tube cooled down to 0° ; a very volatile liquid was thus condensed, colorless at 10° , but green at common temperatures. Peligot found that from the acid thus prepared a dark green liquid might be distilled, boiling at 50° , but containing only 31 per cent. of nitrogen; from this he obtained, by redistillation, an acid boiling at 35° , and containing 33 per cent. of nitrogen;

whence he infers that Liebig's acid is a mixture of the hyponitrous and nitrous acids. According to Fritzsche (*Jour. Prakt. Chem.*, xix. and xxii.) hyponitrous acid is obtained by gradually adding, by means of a tube drawn out to a fine point, 45 parts of water (5 atoms) to 92 parts of nitrous acid (2 atoms) cooled down to 0°, and distilling into a receiver, surrounded by freezing mixture, till the boiling-point rises to 82°.

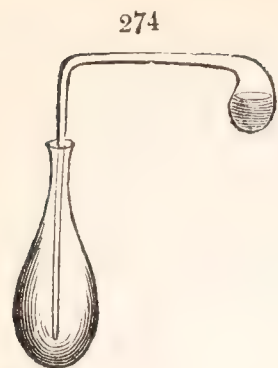
(28° C.) The product is of an indigo-blue color. This is probably pure hyponitrous acid (GMELIN.) Its vapor is orange-colored, and its boiling-point below 82°; but when distilled, it is partially decomposed into nitric oxide and nitrous acid: its aqueous solution is blue. The component volumes of nitrogen and oxygen in hyponitrous acid are, as in the annexed diagram, 1 and 1·5; or it consists of

Nitrogen.	Oxygen.
	8
14	8
	8

Volumes.					
Nitrogen	1	14	36·8
Oxygen.....	3	24	63·2
<hr/>					
Hyponitrous acid....	1		38		100·0

The hyponitrous acid appears to form distinct salts by combining with the salifiable bases. When, for instance, nitrate of potassa or nitrate of baryta are heated, oxygen is evolved, and a soluble *hyponitrite* remains. $KO, NO_5 = KO, NO_3, + 2 O$. When nitric oxide gas is kept for some weeks in contact with a solution of potassa, it is partly converted into nitrous oxide, and the solution yields crystals of *hyponitrite of potassa*; 100 volumes of nitric oxide left 25 of nitrous oxide: the acid, therefore, which was absorbed, consisted of 100 volumes of nitrogen, and 150 of oxygen. According to Berzelius, several of the hyponitrites are best obtained by boiling metallic lead in a solution of nitrate of lead, by which a *hyponitrite of lead* is formed: this salt may then be decomposed by sulphates, which form sulphate of lead, and the hyponitrous acid unites to the base of the original sulphate. Mitscherlich prepares hyponitrites by the mutual action of soluble chlorides and hyponitrite of silver (see SILVER.)

NITROUS ACID. HYPONITRIC ACID. PEROXIDE OF NITROGEN (Graham.) NO_4 or \ddot{N} . When 2 volumes of nitric oxide and 1 volume of oxygen are mixed in an exhausted glass vessel, the gases combine with the evolution of heat consequent upon their mutual condensation, and form *nitrous acid vapor*, which is condensible into a liquid at 0°, and crystallises at a somewhat lower temperature. The specific gravity of this liquid is 1·45; at 32° it is pale yellow; but at 60° deep orange: it boils at 82°, (GAY LUSSAC,) (at 72°, PELIGOT,) and when exposed to the air at common temperature, gradually evaporates in yellow fumes. (DULONG, *Ann. Ch. et Ph.*, ii.) When a mixture of the gases, in the above proportions, is propelled through a tube cooled to 0°, the liquid acid is at once obtained. If the gases be mixed over water, hyponitrous acid and nitric acid are formed at low temperatures; ($2 NO_4 = NO_3, NO_5$,) and at higher temperatures nitric acid and nitric oxide are the results. ($3 NO_4 = 2 NO_5, NO_2$.) The product of the distillation of dry nitrate of lead appears



to be nitrous acid, nearly, if not quite pure and anhydrous; the salt should be put into a small retort, with the beak drawn out, and introduced into a small tube receiver, as in fig. 274, which should be immersed in a freezing mixture: when a sufficient quantity of the liquid acid is collected in it, it may be sealed by applying the flame of a spirit lamp to the elongated neck.

Nitrous acid vapor supports the combustion of phosphorus, and of charcoal, but extinguishes sulphur. Its color, like the liquid acid, varies with the temperature, becoming darker when heated, and paler when cooled; it has a very peculiar odor, which strongly adheres to the hair and to woollen clothing. Nitrous acid does not apparently unite with the bases, but forms with them *hyponitrites* and *nitrates*, hence it has been regarded as a compound of hyponitrous and nitric acids: when passed over baryta and other bases, at a temperature of between 300° and 400° , it is very rapidly absorbed with the evolution of heat, and the products are, according to Gay Lussac, as just stated. (*Ann. Ch. et Ph.*, i.)

Nitrous acid vapor is constituted of 1 volume of nitrogen, and 2

volumes of oxygen condensed into 1 volume; or, as above stated, and as will be apparent from the annexed diagram, of 2 volumes of nitric oxide and 1 volume of oxygen. Its specific gravity, therefore, to hydrogen, will be as 46 to 1; to air, as 3.19 to 1; and 100 cubic inches

Nitrogen.	Oxygen.	
14	8	
	8	
	8	
	8	
=		Nitrous Acid.
		46

will weigh 98.8 grains. It is, therefore, obviously constituted of

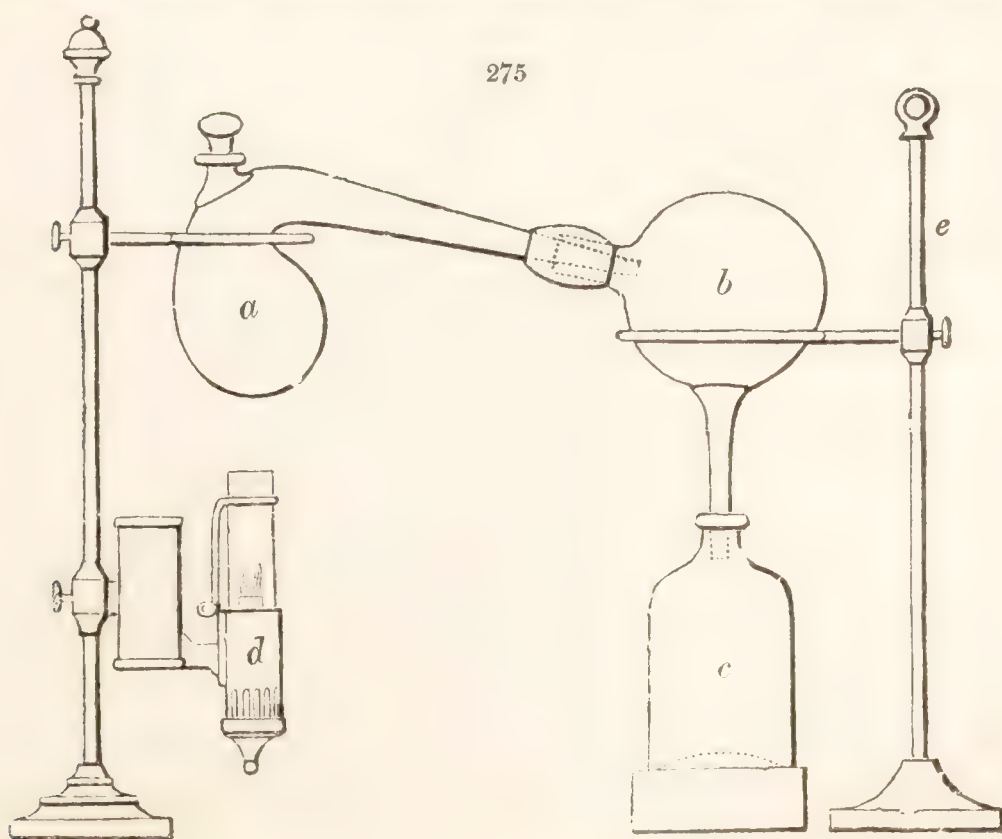
					Dulong.	Peligo.	Vols.	Sp. Gr.					
Nitrogen	1	...	14	...	30.4	...	29.96	...	30.57	...	1	...	0.9706
Oxygen	4	...	32	...	69.6	...	70.04	...	69.43	...	2	...	2.2186
<hr/>													
Nitrous acid....	1		46		100.0		100.00		100.00		1		3.1892

NITRIC ACID. **AZOTIC ACID.** NO_5 , or $\ddot{\text{N}}$; and in its hydrated state, HO, NO_5 , or H, NO_6 . The composition of this acid was first demonstrated by Cavendish, in 1785. (*Phil. Trans.*) He produced it by passing a succession of electric sparks through a mixture of 7 volumes of oxygen and 3 of nitrogen, This experiment has more lately been verified by Faraday (*Experimental Researches*, 3rd Series, § 324,) in reference to the appearance of minute quantities of nitric acid in the rain of thunder storms. Nitric acid is also formed when nitric oxide is slowly added to an excess of oxygen gas, over water. In this way 4 volumes of nitric oxide condense 3 volumes of oxygen; but nitric oxide and oxygen never combine in these proportions without the presence of water, or a base, and *dry nitric acid*, NO_5 , has not been insulated.

Nitric acid (HO, NO_5) is usually obtained by the distillation of purified *nitre* with sulphuric acid, of which materials different proportions are em-

ployed. The nitric acid of commerce, which is generally red and fuming, in consequence of the presence of nitrous acid, is procured by distillation of two parts of nitre with one of sulphuric acid; these proportions afford about one part of orange-colored nitric acid of the specific gravity of 1.48. Upon the large scale, 112lbs. of nitre, and 56 of sulphuric acid, yield from 50 to 52lbs. of nitric acid. Some manufacturers employ three parts of nitre and two of sulphuric acid, and the *London Pharmacopœia* directs equal weights, by which nearly a colorless nitric acid is afforded, provided the distillation be conducted at as low a temperature as possible. Nitrate of soda being cheaper than nitrate of potassa, is also frequently resorted to as a source of nitric acid. "As nitre generally contains a little sea salt, the first portions of acid which distil are impure, containing chlorine and nitrous acid, but they serve to wash quite clean the neck of the retort, on which some sulphuric acid is commonly to be found in spite of all our care, as well as traces of powdered nitre; it is best, therefore, to collect the first portion, say one-tenth of the whole, in a separate receiver, and when the liquid that drops is found to be free from chlorine, (by the test of nitrate of silver,) the receiver is changed, and the rest of the nitric acid is thus obtained quite pure, or, at most, slightly tinged by nitrous acid. By this simple device, we avoid the necessity of redistilling the acid, as commonly directed. The impure portion which first passes over is well adapted for experiments of illustration." (GREGORY.) When 2 equivalents of sulphuric acid (oil of vitriol) to 1 of nitre are used, the results are 1 equivalent of hydrated bisulphate of potassa and 1 of monohydrated nitric acid: $\text{KO}, \text{NO}_5 + 2[\text{SO}_3, \text{HO}] = \text{KO}, \text{HO}, 2\text{SO}_3 + \text{NO}_5, \text{HO}$. When 100 parts of nitre, 96.8 of oil of vitriol, and 40.45 of water are mixed and distilled, at 266° to 270° , nitric acid, of specific gravity 1.4, passes over during the whole process. (MITSCHERLICH.)

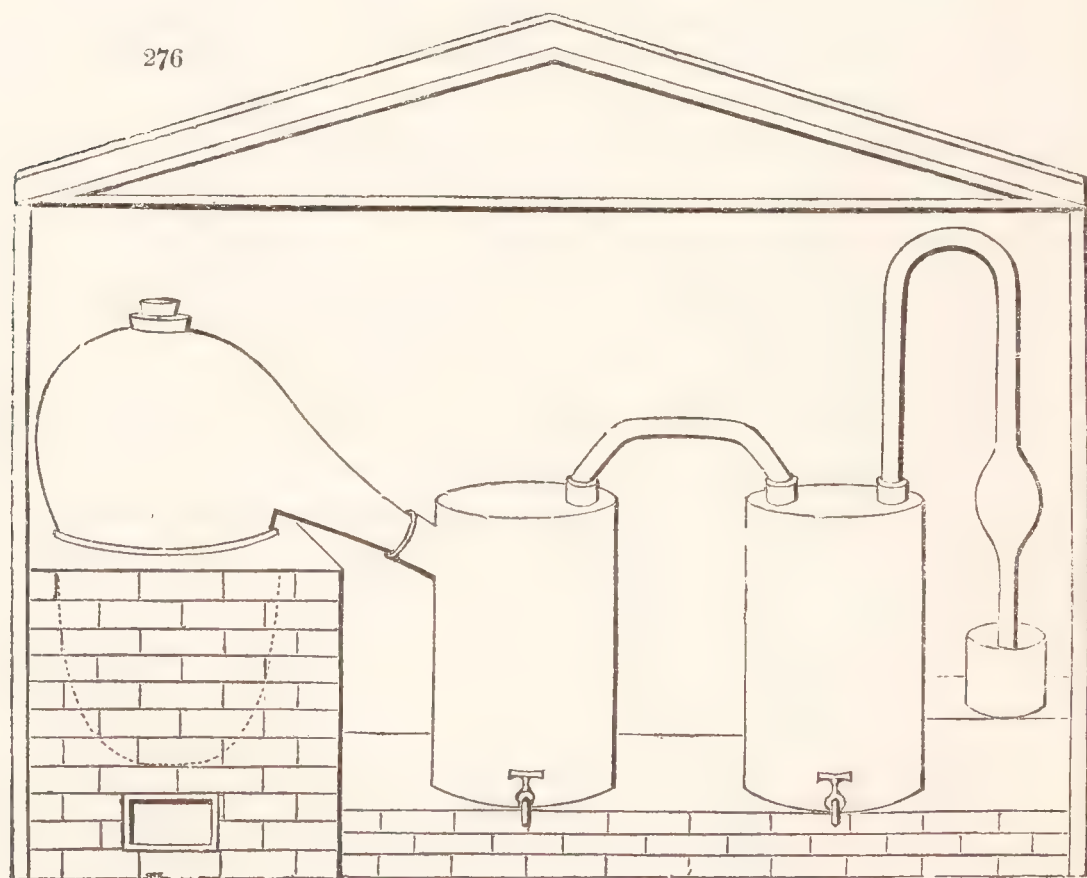
Oil of vitriol of the sp. gr. 1.84, contains one equivalent of dry sulphuric acid and *one* of water; whereas liquid nitric acid usually contains one equivalent of dry acid and *two* of water: hence the requisite excess of oil of vitriol, where colorless and perfect nitric acid is to be



obtained; hence, too, the red color of the acid of commerce, in consequence of the smaller quantity of oil of vitriol generally used by the manufacturer, the deficiency of water occasioning the nitric acid to be resolved into nitrous acid and oxygen. This will be more apparent by reference to the article *Bisulphate of Potassa*.

The distillation of nitric acid may be conducted upon the small scale in a tubulated glass retort *a*, with a tubulated receiver *b*, passing into the bottle *c*, as shown in the preceding wood-cut. The requisite heat is obtained by the lamp *d*, and the whole apparatus supported by the brass stands with sliding rings *e e*.

But the manufacturer who prepares nitric acid upon a large scale, generally employs distillatory vessels of stone ware. The following wood-cut represents the arrangement of the distillatory apparatus for the production of common *aqua fortis*: it consists of a pot set in brick-work, over a fire-place; an earthen head is luted upon it, communicating with two or more receivers of the same material, furnished with earthen-ware stop-cocks, the last of which has a tube of safety dipping into a basin of water. The second receiver contains water, and in it the nitrous vapors are condensed, the stronger acid being collected in the first.



The nitric acid, or aqua fortis of commerce, is always impure, and hydrochloric and sulphuric acids may generally be found in it. The former may be detected by *nitrate of silver*, and the latter by a dilute solution of *nitrate of baryta*. If, however, pure nitre and pure sulphuric acid be employed in its production, and the latter not in excess, there is little apprehension of impurity in the resulting acid. If the acid is colored by the presence of nitrous acid, it is rendered colorless by boiling, which is best performed in a retort, with a loosely-attached receiver: the nitrous acid passes off. If it contain hydrochloric acid this is also decomposed by boiling, and chlorine escapes.

Pure and perfect nitric acid is a colorless liquid, extremely sour and corrosive, and very intense in its action upon the greater number of inflammable bodies, to which it imparts oxygen, and by which it is resolved into some of the inferiorly-oxidized compounds. Its specific gravity, as usually obtained, fluctuates between 1·4 and 1·5. At 247°, when of the specific gravity 1·40, it boils and distils over without change, but the dilute acid is strengthened by boiling; and the strongest acid boils at a lower temperature than that which is of a somewhat less specific gravity. The following table of boiling-points has been given by Mr. Dalton, which shows that the boiling-point of the acid of the specific gravity 1·42, composed of 1 atom of real acid and 4 atoms of water, is the maximum. This is called by Mr. Graham “the proper *nitrate of water*; and of the four atoms of water which it contains, one is combined with the acid, as base, and may be named *basic water*, while the other three are in combination with the nitrate of water, and may be termed the *constitutional water* of the salt.” He represents this acid in symbols, thus, $\text{HO}, \text{NO}_5 + 3 \text{HO}$.

Acid of specific gravity 1·50 boils at 210°				Acid of specific gravity 1·35 boils at 242°			
”	1·45	”	240	”	1·30	”	236
”	1·42	”	248	”	1·20	”	226
”	1·40	”	247	”	1·15	”	219

At -40° the concentrated acid congeals. When diluted with half its weight of water it freezes at about -2° . When the acid of 1·45 is exposed to the air it exhales fumes of a peculiar odor, and gradually absorbs water, so that its bulk becomes increased, and its specific gravity ultimately diminished. It suffers a partial decomposition when exposed to light, becoming yellow and evolving oxygen, so that it should be kept in a dark place, and especially excluded from the direct rays of the sun. By distilling nitric acid (sp. gr. 1·4) twice successively from four times its weight of sulphuric acid, Gay Lussac increased its density to 1·510. In this state he found it remarkably susceptible of decomposition by heat or light. (*Ann. Ch. et Ph.*, i.) According to Thenard, a mixture of 1 part of nitric and 4 of sulphuric acid, gently heated, affords oxygen and nitrous acid, the sulphuric acid becoming diluted by the abstraction of the water of the nitric acid.

When nitric acid is mixed with snow, the latter is suddenly liquified, and intense cold is produced. Nitric acid, of the sp. gr. 1·5, mixed with half its bulk of water, occasions an elevation of temperature in the mixture $= 112^\circ$: 58 parts of the acid with 42 of water, both at 60° , give, on mixture, a temperature of 140° . (URE, *Quarterly Journal*, iv. 298.) On diluting the red fuming acid it assumes various tints of bluish green dependent upon the quantity of water added.

Nitric acid has not, as already stated, been obtained in an anhydrous state; the liquid acid being a compound of the anhydrous acid and water, or, in the language of Mr. Graham, a *nitrate of water*; the salts called *nitrates*, (such as *nitrate of potassa*,) are compounds of the anhydrous acid and a salifiable base. *Anhydrous nitric acid* is constituted of one volume of nitrogen and two volumes and a half of oxygen, as in the annexed diagram.

Nitrogen.	Oxygen.
14	8
	8
	8
	8
	8

It is therefore a compound of

	Lavoisier.			Cavendish.			Berzelius.		
Nitrogen.....	1	14	25.9	20	25	26			
Oxygen	5	40	74.1	80	75	74			
	1	54	100.0	100	100	100			

The liquid nitric acid in its utmost state of concentration (sp. gr. 1.5), consists, according to Phillips, of one equivalent of anhydrous acid and one and a half of water. According to Dr. Ure, the acid of a specific gravity of 1.486 contains one equivalent of real acid and two of water: hence the following table:—

	Sp. gr. = 1.5.				Sp. gr. = 1.486.			
Anhydrous acid.....	1	54	80		1	54	75	
Water	1½	13.5	10		2	18	25	
	1	67.5	100		1	72	100	

The following table, drawn up by Dr. Ure, exhibits the quantity of dry acid and of liquid acid (sp. gr. 1.5) at different densities; (*Quarterly Journal*, iv. 297, and *Dictionary*, p. 71, sec. edit. ;) the quantity of anhydrous acid in the liquid acid of sp. gr. 1.50 being assumed = 79.7. The column of dry acid shows the weight which any salifiable base would gain by uniting, so as to form an anhydrous salt, with 100 parts of the liquid acid of the corresponding specific gravity.

Specific gravity	Liquid acid in 100.	Dry acid in 100.	Specific gravity.	Liquid acid in 100.	Dry acid in 100.	Specific gravity.	Liquid acid in 100.	Dry acid in 100.
1.5000	100	79.700	1.3783	66	52.602	1.1895	33	26.301
1.4980	99	78.903	1.3732	65	51.805	1.1833	32	25.504
1.4960	98	78.106	1.3681	64	51.068	1.1770	31	24.707
1.4940	97	77.309	1.3630	63	50.211	1.1709	30	23.900
1.4910	96	76.512	1.3579	62	49.414	1.1648	29	23.113
1.4880	95	75.715	1.3529	61	48.617	1.1587	28	22.316
1.4850	94	74.918	1.3477	60	47.820	1.1426	27	21.519
1.4820	93	74.121	1.3427	59	47.023	1.1465	26	20.722
1.4790	92	73.324	1.3376	58	46.226	1.1403	25	19.925
1.4760	91	72.527	1.3323	57	45.429	1.1345	24	19.128
1.4730	90	71.730	1.3270	56	44.632	1.1286	23	18.331
1.4700	89	70.933	1.3216	55	43.835	1.2217	22	17.534
1.4670	88	70.136	1.3163	54	43.038	1.1168	21	16.737
1.4640	87	69.339	1.3110	53	42.241	1.1109	20	15.940
1.4600	86	68.542	1.3056	52	41.444	1.1051	19	15.143
1.4570	85	67.745	1.3001	51	40.647	1.0993	18	14.346
1.4530	84	66.948	1.2947	50	39.850	1.0935	17	13.549
1.4500	83	66.155	1.2887	49	39.053	1.0878	16	12.752
1.4460	82	65.354	1.2826	48	38.256	1.0821	15	11.955
1.4424	81	64.557	1.2765	47	37.459	1.0764	14	11.158
1.4385	80	63.760	1.2705	46	36.662	1.0708	13	10.361
1.4346	79	62.963	1.2644	45	35.865	1.0651	12	9.564
1.4306	78	62.166	1.2583	44	35.068	1.0595	11	8.767
1.4269	77	61.369	1.2523	43	34.271	1.0540	10	7.970
1.4228	76	60.572	1.2462	42	33.474	1.0485	9	7.173
1.4189	75	59.775	1.2402	41	32.677	1.0430	8	6.376
1.4147	74	58.978	1.2341	40	31.880	1.0375	7	5.579
1.4107	73	58.181	1.2277	39	31.083	1.0320	6	4.782
1.4065	72	57.384	1.2212	38	30.286	1.0267	5	3.985
1.4023	71	56.587	1.2148	37	29.489	1.0212	4	3.188
1.3978	70	55.790	1.2084	36	28.692	1.0159	3	2.391
1.3945	69	54.993	1.2019	35	27.895	1.0106	2	1.594
1.3882	68	54.196	1.1958	34	27.098	1.0053	1	0.797
1.3833	67	53.399						

Dr. Thomson has constructed the following table showing the specific gravity of various atomic combinations of nitric acid and water.

Atoms of Acid.	Atoms of Water.	Acid in 100 parts.	Specific Gravity.
1	1	85·714	1·5500
1	2	75·000	1·4855
1	3	66·668	1·4546
1	4	60·000	1·4237
1	5	54·545	1·3928
1	6	50·000	1·3692
1	7	46·260	1·3456
1	8	42·857	1·3220
1	9	40·000	1·3032
1	10	37·500	1·2844
1	11	35·294	1·2656
1	12	32·574	1·2495
1	13	31·579	1·2334
1	14	30·000	1·2173
1	15	28·571	1·2012

Nitric acid may be decomposed by passing its vapor through a red-hot porcelain tube; oxygen is given off, nitrous acid vapor is produced, and a quantity of diluted acid passes over into the receiver, having escaped decomposition; so that it is thus proved to consist of nitrous acid, oxygen, and water. At a white heat, oxygen, nitrogen, and water, only, are evolved. When strong nitric acid was electrolysed, no gas appeared at the negative electrode, but nitrous acid, and apparently nitric oxide, were formed there, which rendered the acid red and effervescent. In dilute nitric acid, gas appeared at the negative electrode, its quantity being varied by variations either in the strength of the acid or of the voltaic current: the gas at the anode was always oxygen, that at the cathode, hydrogen. When the quantity of products was examined by the voltameter, the oxygen, whether from strong or weak acid, was always in the same proportion as from water. When the acid was diluted to sp. gr. 1·24 or less, the hydrogen also proved to be in the same quantity as from water; hence Faraday concludes, that nitric acid does not undergo electrochemical decomposition, but the water only: that the oxygen at the anode is always a primary result, but that the products at the cathode are often secondary, and due to the reaction of the hydrogen upon the acid. (*Phil. Trans.*, 1834, p. 96.)

According to Daniell the result of the electrolysis of nitric acid, composed of 1 atom of anhydrous acid and 1 of water, is attended by the evolution of hydrogen at the cathode, and of a compound (which he calls *oxynitron*) of 1 atom of nitrogen and 6 of oxygen, at the anode; hence HO, NO_5 , becomes in such case NO_6, H . (*Phil. Trans.*, 1840, p. 223.) These results of the electrolysis of the nitric and other hydrated acids importantly affect our theoretical notions of their constitution; thus it is obvious that liquid nitric acid may either be represented as a hydrate of a hypothetical dry acid, and this is the usual view; or it may be considered as a compound of hydrogen with the hypothetical base NO_6 . The advantage of the latter view is that it assimilates the hydrated oxyacids and their salts, with the hydracids and their salts. If, for instance, nitric acid be represented as $\text{H} + \text{NO}_6$ instead of $\text{HO} + \text{NO}_5$, (or as Graham calls it, a *nitrate of water*), then nitrate of potassa will be

$K + NO_6$ instead of $KO + NO_5$; that is, the atom of hydrogen in the acid, is replaced in the salt by an atom of potassium. In the hydracids, take for instance the hydrochloric, $H + Cl$, the hydrogen is similarly replaced by a metal in the formation of their salts, chloride of potassium being $K + Cl$.: it is obvious that here, the compound body NO_6 is regarded as performing the functions of the supposed elementary body Cl . These views originated with Davy, and have recently been adopted by several eminent chemists.

When nitric oxide is passed through concentrated nitric acid, it is decomposed, and nitrous acid is formed, partly by the acquisition of oxygen by the oxide, and partly by its loss by the acid. Dr. Turner observes, that "The nitrous acid thus derived from two sources gives a color to the nitric acid, the depth and kind of which depend upon the quantity of the deutoxide of nitrogen which has been employed. The first portion communicates a pale straw-color, which gradually deepens as the absorption of the deutoxide continues, till the nitric acid has acquired a deep orange hue, together with all the characters of strong, fuming nitrous acid. But the solution still continues to absorb the deutoxide, and, in doing so, its color passes through different shades of olive and green, till it becomes greenish-blue. By applying heat to the blue liquid, the deutoxide of nitrogen is evolved, and in proportion as it escapes, the color of the solution changes to green, olive, orange, and yellow; at length becoming pale as at first. Nitrous acid vapors are likewise disengaged as well as the deutoxide. These phenomena are very favorable to the view that the conversion of the orange-color into olive, green, and blue, is owing to the formation of hyponitrous acid." (*Elements of Chem.*, 5th ed., 290.)

Some of the metals, such as copper, tin, and silver, are at first without action on concentrated nitric acid, but become vehemently active upon the addition of a little water. Poured upon hot iron-filings or melted bismuth, zinc, or tin, nitric acid causes a combustion of the metals. In acting upon the metals which decompose water, nitric acid gives rise to the formation of ammonia, and nitrate of ammonia is among the results, a fact long ago noticed by Payen, Pelletier, and Guyton-Morveau, and more lately examined by Kuhlmann, and by Fordos and Gélis. (*Ann. Ch. et Ph.*, Juillet, 1843.) No ammonia is formed during the action of nitric acid on copper, lead, antimony, bismuth, mercury, or silver.

The facility with which nitric acid imparts oxygen, renders it a valuable oxidizing agent. Phosphorus decomposes it at common temperatures, and sulphur and carbon, when aided by heat. A piece of glowing charcoal thrown upon the surface of the concentrated acid, burns vehemently with the evolution of red fumes. (BERZELIUS.) It acts energetically (often, when diluted,) upon the greater number of organic bodies, and mutual decompositions ensue. A drachm of oil of turpentine mixed with half a drachm of sulphuric acid, instantly bursts into flame upon the addition of a drachm of nitric acid. Malic, oxalic, and carbonic acids, are the common products of the action of dilute nitric acid upon many vegetable and animal substances: ammonia, and hydrocyanic acid are also sometimes formed. It tinges many animal substances of a yellow color, and permanently stains the nails and cuticle; it is hence employed in the production of yellow patterns upon

colored woollen goods. It is used in fumigations to destroy contagious and infectious matter, more especially where chlorine would prove injurious; for this purpose nitrate of potassa and sulphuric acid are mixed in a saucer, and the evolution of the acid vapor aided by a gentle heat; but it is not so effective as chlorine. In pharmacy, and a variety of other processes, it is susceptible of interesting applications: it is used for etching on copper, and as a solvent for tin in the preparation of valuable mordants used by dyers and calico printers: it is an important agent in metallurgy, and especially in the art of assaying. In medicine it is prescribed as a tonic; and occasionally in syphilitic, hepatic, and eruptive disorders; and in surgery as an energetic caustic. In the bite of rabid animals, if effectually applied to the wound, there is every reason to believe that it would destroy the poison and prevent its consequences.

As the salts of nitric acid are all soluble in water, neither its presence nor quantity can be determined by any precipitating re-agent. When uncombined, it is recognised by the facility with which it attacks copper, causing the evolution of nitric oxide, and affording a blue solution; and by the formation of *nitre*, when it is saturated with potassa, which salt readily crystallizes in long six-sided prisms. When hydrochloric acid is added to a solution of a *nitrate*, chlorine is evolved, and the liquid acquires the power of dissolving gold-leaf; but as the action of hydrochloric acid on the salts of chloric and bromic acid also furnishes a solution which dissolves gold, no inference can be drawn from the experiment, except the absence of those acids has been previously ascertained.

The following method of detecting the presence of nitric acid has been suggested by Liebig, who says that it is effective when not more than a four-hundredth part of the acid is present. The liquid to be examined must be mixed with a sufficiency of sulphuric solution of indigo, to acquire a distinct blue color; a few drops of concentrated sulphuric acid are then added, and the whole boiled; if the liquid contain a nitrate, it will either be bleached or rendered yellow. By adding a little common salt to the liquid before applying heat, a five-hundredth part of nitric acid may be discovered. (*Ann. Ch. et Ph.*, xxxv. 80.)

M. Runge proposes to detect nitric acid and its combinations as follows:—"Pour a solution of protochloride of iron upon the surface of an amalgam of zinc, and then place a crystal of nitre on the latter in the fluid: a dark band immediately forms around the crystal, sometimes extending over the whole surface of the amalgam. All the nitrates, as well as nitric acid, act in this manner; but other salts, such, for instance, as the chlorates, produce no such effect, so that a very sensible test of the presence of nitric acid is thus afforded. It is necessary that the solution employed be a protosalt of iron. If nitric acid is supposed to exist in a liquid, it should be saturated with potassa, evaporated to dryness, and the dry mass tried. Salts of copper and silver must not be present." (*Annalen der Physik*, 1827.)

Another test for nitric acid has been proposed by Richemont: the liquid suspected to contain a nitrate is mixed with an equal bulk of sulphuric acid, and when cool a few drops of a strong solution of protosulphate of iron are added; nitric oxide is evolved, which produces a purplish tint, even when the quantity of nitric acid is very small. Dr. Turner observes that another character which may be useful consists in

mixing the supposed nitric acid or nitrate with dilute sulphuric acid, in a tube, adding a few fragments of zinc, and setting fire to the hydrogen as it issues; if nitric acid be present the flame of the hydrogen will have a greenish-white tint, due to the admixture with binoxide of nitrogen. "A very delicate test," he adds, "has been proposed by O'Shaugnessy, founded on the orange-red, followed by a yellow color, which nitric acid communicates to morphia. The supposed nitrate is heated in a test tube with a drop of sulphuric acid, and then a crystal of morphia is added. It is advisable to try the process in a separate tube with the sulphuric acid alone, in order to prove the absence of nitric acid in it."

Nitric acid is an important agent in the operations of analysis. It is used,—1. to oxidize and dissolve the metals, and to separate them from the few which are not acted upon by it, especially gold and platinum: it is of constant use in the process of assaying, for separating silver from gold. 2. To separate certain metals in the form of insoluble peroxides, such as antimony and tin, from those which yield soluble oxides, as in the separation of tin from mercury; it also is useful in the peroxidization of iron and manganese, by which those metals are rendered insoluble in nitric acid, and thus separable from soluble earths, &c. 3. Dilute nitric acid separates sulphur from the metals in the form of an insoluble magma, or grey powder, as in the analysis of sulphuret of copper, of lead, or of silver; if concentrated, it acidifies sulphur and arsenic. 4. The concentrated acid detects sulphuretted hydrogen by the production of a white cloud, and the destruction of its fetid odor. 5. It is used as a solvent to determine the nature of certain precipitates, and to separate the soluble from the insoluble. The precipitates formed by the vegetable acids, by succinic acid, by phosphoric acid, and by arsenic acid in the solutions of baryta, of lime, and of lead, are soluble in dilute nitric acid; but the precipitate by sulphuric acid in solutions of baryta is insoluble, and that in solution of lead difficultly soluble, requiring about 100 parts of the acid. 6. Nitric acid is a test of certain organic substances: it generally tinges those containing nitrogen of a yellow color; it detects strychnia, by rendering it red; the nitric solution of uric acid leaves a red residue on evaporation; it changes polychroite to green, and guaiacum to blue and green. It distinguishes gum from starch, by converting the former into mucous or saccharic acid: cork it converts into suberic acid. 7. Many of the nitrates, and the nitrohydrochloric acid, are used as tests. (PFAFF. *Handbuch der Analytischen Chemie*, i. 98, 2nd ed.)

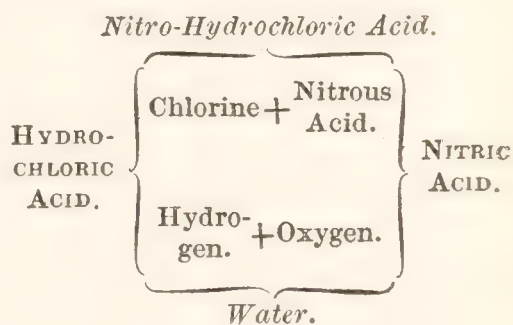
Nitrates. Most of these salts are neutral, corresponding with the general formula $MO + NO_5$; or upon the binary theory $= M + NO_6$. Their general properties will be described afterwards. They are decomposed when gently heated with oil of vitriol, evolving fumes of nitric and nitrous acid; they also deflagrate with red-hot charcoal, forming carbonates, and giving off carbonic acid gas. Graham observes, with respect to the nitrates of the magnesian class, that they all contain water in intimate combination, so that 1 equivalent of it appears to be essential to the salt, and their formula is analogous to that of the nitric acid itself. It has been above stated that of the 4 atoms of water which nitric acid, sp. gr. 1.42, contains, 1 is combined with the acid as base, and therefore termed *basic water*, while the other 3 are in combination

with the nitrate of water, and form the *constitutional water* of that salt. The same 3 atoms of constitutional water are found in all the magnesian nitrates, with the addition often of another 3 atoms of water, as appears from the following formulæ:—

Nitric acid (1·42)	HO, NO ₅ + 3 HO
Prismatic nitrate of copper	CuO, NO ₅ + 3 HO
Rhomboidal nitrate of copper	CuO, NO ₅ + 3 HO + 3 HO
Nitrate of magnesia	MgO, NO ₅ + 3 HO + 3 HO

The proportion of water in the nitrate of magnesia may be reduced, by heating the salt, to 1 atom, leaving the compound MgO, NO₅ + HO, but on urging the temperature still higher, the last atom of water and the acid are expelled together, and magnesia is left behind; neither this nor any other nitrate of the magnesian class being capable of existing without an atom of water. There are no double nitrates, nor are there any nitrates with excess of acid.

NITRO-HYDROCHLORIC ACID. NITRO-MURIATIC ACID. This term has been applied to the *Aqua Regia* of the alchemists. When nitric and hydrochloric acids are mixed, they become yellow, and acquire the power of dissolving gold, which neither of the acids possessed separately. This mixture evolves chlorine, a partial decomposition of both acids having taken place, and water, chlorine, and nitrous acid are thus produced; that is, the hydrogen of the hydrochloric acid abstracts oxygen from the nitric to form water: the result must be chlorine and nitrous acid. (DAVY, *Journal of Science and the Arts*, vol. i. p. 67.) The annexed diagram may, perhaps, serve to render these mutual changes more evident. Two parts of hydrochloric and one of nitric acid furnish the most effective mixture; but a solution having the same general properties is obtained by adding nitre to hydrochloric acid, or common salt to nitric acid. The mutual decomposition of the two acids proceeds only so far in the first instance as to saturate the liquid with chlorine; but when heat is applied, chlorine is evolved till one of the acids is entirely decomposed. When a metal is put into nitro-hydrochloric acid, it absorbs the chlorine, and is dissolved; for the liquid cannot become then saturated with chlorine, because the metal combines with it as fast as it is evolved: the application of heat greatly accelerates this action, but much chlorine may be lost by employing too high a temperature. As nitric oxide is evolved during the solution of a metal in nitro-hydrochloric acid, it might be supposed that the hydrogen of the hydrochloric acid had reduced the nitric acid to the state of nitric oxide; but Davy has shown that a mixture of hydrochloric and *nitrous* acids possesses none of the properties of *Aqua Regia*: consequently, the evolution of nitric oxide depends upon the spontaneous resolution of the produced nitrous acid into nitric acid and nitric oxide. Nitro-hydrochloric acid is the common solvent of gold and platinum, and may, with proper precautions, be used in the separation of those metals from silver, which remains as an inso-

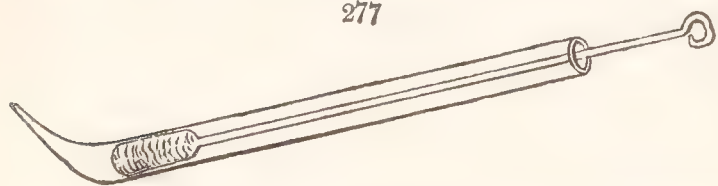


luble chloride. It furnishes a useful solution of tin; and is employed in the analysis of minerals containing sulphur, to separate and acidify that elementary body. During the solution of metals in this acid, the formation of nitric oxide gas, and a metallic chloride is as follows:— $3M, NO_5, 3HCl = 3MCl, 3HO, NO_2$.

NITROGEN AND CHLORINE. CHLORIDE OF NITROGEN. TERCHLORIDE OF NITROGEN. NCl_3 . The gases do not unite *directly*, but the compound may be obtained by exposing a solution of *nitrate* or *hydrochlorate of ammonia* to the action of chlorine, at a temperature of 60° or 70° . The gas is absorbed, and an oil-like fluid, heavier than water, is produced by the union of the nascent nitrogen (evolved in the decomposition of the ammonia of the salt) with the chlorine. $NH_3, HCl, + 6Cl = 4HCl + NCl_3$. It was discovered by Dulong, in 1812 (*Ann. de Chim.*, LXXXV.,) and its properties afterwards investigated by Davy. (*Phil. Trans.*, 1813. See also SERULLAS, *Ann. Ch. et Ph.*, XLii. 200; and MILLON, *ibid.*, LXIX. 75.)

The simplest mode of obtaining this compound consists in filling a perfectly clean glass basin with a solution of 1 part of sal-ammoniac in 12 or 15 of water, and inverting into it a tall jar of chlorine. The saline solution is gradually absorbed, and rises into the jar, a film forms upon its surface, and it acquires a yellow color: at length small globules, looking like yellow oil, collect upon its surface, and successively fall into the

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basin beneath, whence they are most conveniently removed by drawing them into a small and perfectly clean glass syringe, made of a glass tube drawn to

pointed orifice (fig. 277,) and having a copper-wire with a piece of clean tow wrapped round it for a piston; in this way a globule may be drawn into the tube, and transferred to any other vessel. Balard obtained this compound by suspending a piece of sulphate of ammonia in a strong solution of hypochlorous acid.

The specific gravity of chloride of nitrogen is 1.65; it is not congealed by cold. Its odor is irritating and peculiar; it very soon evaporates when exposed to air. It is apparently a non-conductor of electricity. It is dangerously explosive, and is decomposed with violent detonation by many combustibles, especially phosphorus and fixed oils. In making these experiments, which should be conducted with extreme caution, and the face protected by a mask, (Dulong lost an eye and the use of a finger, and Sir H. Davy was wounded in the face, by the effects of its detonation,) a small globule of the compound, about the size of a mustard seed, may be cautiously transferred to a clean porcelain basin, half filled with water, and placed under a wire-cage: a very small piece of phosphorus, fixed to the end of a long stick, or a long rod with the extremity dipped in oil, may be then brought into contact with the globule, which instantly explodes with a flash of light, dispersing the water, and breaking the basin to atoms. At 160° it distils without change, but at 212° it explodes, and is decomposed. It was submitted to the action of 125 different substances, by Messrs. Porret, Wilson, and Kirk, of which the following caused it to explode.

Phosphorus	Linseed-oil	Oil of orange peel
Phosphuret of lime	Olive-oil	Naphtha
Caoutchouc	Camphorated oil	Strong liquid ammonia
Myrrh	Sulphuretted oil	Fused potassa
Palm-oil	Oil of turpentine	Phosphuretted hydrogen
Ambergris	Oil of tar	Nitric oxide
Whale-oil	Oil of amber	Metallic soaps.

The metals, resins, and sugar, did not cause it to explode. (NICHOLSON'S *Journal*, vol. xxxiv.) Alcohol quietly changes it into a white substance. Mercury, and most of the other metals, absorb the chlorine, and evolve nitrogen. It gradually disappears when kept in a stopped phial with water, and nitrous and hydrochloric acids are formed by the mutual decomposition of the liquids. In concentrated hydrochloric acid it forms ammonia, and chlorine is evolved. It is also slowly decomposed by dilute liquid ammonia; hydrochlorate of ammonia is formed, and nitrogen evolved. It dissolves sulphur, and mixes, without explosion, with sulphuret of carbon.

The existence of nitrogen in nearly all the powerfully-detonating bodies is a singular fact, and the decomposition of this compound is attended by a circumstance observed in some other cases, namely, the appearance of flame or fire, which is here, not the result of condensation and union, but is accompanied by expansion and decomposition; by the separation of two bodies previously combined: the decomposition of the oxides of chlorine already referred to, and that of iodide of nitrogen and of peroxide of hydrogen (oxygenated water), exhibits the same peculiarity.

Chloride of nitrogen appears to yield, by decomposition, 1 volume of nitrogen and 3 of chlorine (and not 4, as originally inferred by Davy); and as the specific gravity of nitrogen to chlorine is as 14 to 36, so it may be said to consist of 1 volume of nitrogen + 3 volumes of chlorine, and, in the state of vapor, it is probable that the four volumes of æriform matter which it affords by decomposition, are condensed into one. It is, therefore regarded as a compound of

Nitrogen.	Chlorine.	
14	36	
	36	=
	36	122

Nitrogen	1	14	11.5
Chlorine	3	108	88.5
Chloride of nitrogen	1	122	100.0

From the experiments of Millon, it seems probable that this compound may contain hydrogen.

NITROGEN AND IODINE. IODIDE OF NITROGEN. TRIIODIDE OF NITROGEN. NI₃. This compound may be procured by pouring a solution of ammonia upon a very small quantity of iodine. The iodine decomposes part of the ammonia, and, combining with its hydrogen, forms hydriodic acid, and this, uniting with the ammonia, forms hydriodate of ammonia: the nascent nitrogen unites with another portion of iodine, and

forms an insoluble black powder, which may be collected by pouring off the liquid, and placing it, while moist, in small separate parcels upon bibulous paper, where it must be suffered to dry spontaneously. $4\text{NH}_3 + 6\text{I} = 3[\text{NH}_3, \text{HI}] + \text{NI}_3$. This curious compound was discovered by Courtois. Serullas obtains it by agitating alcoholic solution of iodine with excess of ammonia; it subsides on dilution with water, and must be carefully dried; in this state it does not detonate whilst moist, but if it be put into pure ammonia it explodes when slightly pressed in that liquid. (*Ann. Ch. et Ph.*, XLii. 201.) Mitscherlich (POGGENDORFF'S *Annalen*, xiv. 539) has described another method of obtaining this compound. A chloride of iodine is formed by dissolving iodine in nitro-hydrochloric acid; this solution, saturated with ammonia, yields hydrochlorate of ammonia and iodide of nitrogen: the latter may be collected upon a filter, and separated, whilst moist, into small portions; but it is not safe to operate upon more than a few grains of iodine. In this experiment no gas is evolved; one equivalent of ammonia reacts upon three equivalents of chloride of iodine, so that a volume of nitrogen combines with three volumes of iodine vapor to produce the detonating compound, and three volumes of hydrogen combine with three of chlorine to form hydrochloric acid.

Iodide of nitrogen, when dry, detonates upon the slightest touch, and the detonation of one portion generally causes the neighbouring ones to explode also. When it detonates, the purple fumes of iodine are perceptible. When left exposed to air it slowly evaporates; and if moist, is gradually resolved into nitrogen or ammonia, and iodic and hydriodic acids. It is decomposed by hot water and by alkaline solutions, and by sulphuretted hydrogen. Marchand has attempted to show that this compound contains hydrogen (*Ann. Ch. et Ph.*, LXXiii. 222), but from Gay Lussac and Colin's researches (*Ann. de Ch.*, xci. 30), it appears to consist of

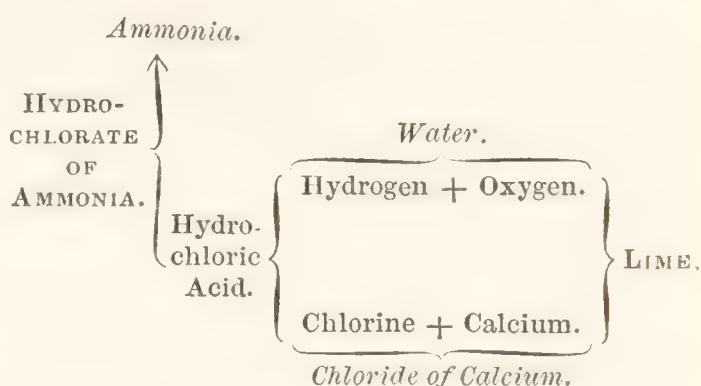
Nitrogen	1	14	3·57
Iodine	3	378	96·43
<hr/>					
Iodide of nitrogen	1		392		100·00

BROMIDE OF NITROGEN. NBr_3 , is obtained, according to Millon, (*Ann. Ch. et Ph.*, LXix. 75,) by gradually adding a solution of an alkaline bromide to the chloride of nitrogen under a thin stratum of water: with bromide of potassium, for instance, bromide of nitrogen and chloride of potassium are the results. Bromide of nitrogen is of dark red color, and more readily decomposed than the chloride: it has an oily aspect, is heavy, very volatile, and its vapor fetid and very irritating to the eyes. Phosphorus and arsenic cause it to detonate with great violence: its general characters are analogous to those of the chloride. According to Millon it contains hydrogen, but its composition is probably the counterpart of that of the chloride of nitrogen and of iodine.

NITROGEN AND HYDROGEN. AMMONIA. VOLATILE ALKALI. TERHYDRURET OF NITROGEN. NH_3 . According to Kane, ammonia is an AMIDIDE OF HYDROGEN $= \text{NH}_2, \text{H}$. When nitrogen and hydrogen gases are mixed, they show no tendency to combine; they unite, however,

under peculiar circumstances of evolution, and the result is *ammonia*. This gaseous compound may be obtained from a mixture of two parts of dry quicklime and one of hydrochlorate of ammonia, introduced into a small retort, and gently heated. It must be collected over mercury. Towards the latter part of the operation a little water goes over, which may be arrested in the neck of the retort by the previous introduction of a piece of blotting-paper; or it may be prevented passing over by filling up the bulb of the retort with powdered lime. Hydrochlorate of ammonia is a compound of hydrochloric acid and ammonia; by the action of the lime (which is an oxide of calcium) the ammonia is expelled in its pure and gaseous form: the hydrochloric acid and the lime then mutually decompose each other, and water and chloride of calcium are the results.

$\text{CaO} + \text{NH}_3, \text{HCl} = \text{CaCl} + \text{HO} + \text{NH}_3$. The annexed diagram may, perhaps, more clearly explain this formula.



Ammonia is permanently elastic at common temperatures; by exposing it to intense cold, Guyton supposed that he had observed it to assume a liquid form. (*Ann. de Chim.*, xxix. 290.) But this could not be the case, as it requires for its liquifaction a pressure of 6·5 atmospheres at the temperature of 50°. (FARADAY, *Phil. Trans.*, 1823, p. 196.) It was most readily obtained in this state by disengaging it by heat, in a sealed tube, from chloride of silver which had been previously saturated with it. It was colorless, transparent, of a specific gravity of 0·76, and its refractive power surpassed that of water. When free from water, it does not conduct electricity. At 103° below 0° this liquified ammonia becomes a white, translucent crystalline solid, heavier than the liquid. The tension of its vapor at 0° is 2·48 atmospheres, at 32°, 4·44 atmospheres, and at 60°, 6·9 atmospheres. (FARADAY, *Phil. Trans.*, 1845, p. 170.)

Gaseous ammonia is pungent and acrid, and of course unrespirable, but when diluted by mixture with common air, it is an agreeable nasal stimulant. The inhalation of highly diluted ammonia, as by respiring air which has been passed over or through a weak solution of it, has been found to relieve chronic hoarseness and other tracheal and bronchial affections. (SMEE, *Med. Gaz.*, April 7, 1843.) It converts most vegetable blues to green, and yellows to red, properties which belong to the bodies called *alkalis*. Ammonia, therefore, has been termed *volatile alkali*; and the change of color thus effected by it, is distinguished from that produced by the *fixed* alkalis, by the return of the original tint, when the ammonia flies off by exposure. Dry ammonia has no action on dry vegetable colors. (KANE.) It saturates the acids, and produces an important class of *ammoniacal salts*, which are recognized by the evolution of ammonia when they are triturated with potassa, soda, or lime.

The specific gravity of ammonia compared with hydrogen is as 8·5 to 1; compared with air it is as 0·5893 to 1; 100 cubical inches weigh 18·268 grains; or, at the temperature of 32°, 19·301 grains. (THOMSON.) It extinguishes flame, but forms a difficultly inflammable mixture with

common air, and may be burned when issuing from a capillary orifice in an atmosphere of oxygen. When mixed with its volume of oxygen it burns with a feeble explosion. Ammonia is abundantly absorbed by chloride of calcium, as well as by several other chlorides, with which, and with the other haloids, it forms a series of compounds which will afterwards be noticed. If it be required artificially to dry the gas, potassa or lime should be used. (*Quarterly Journal*, v. 74.)

Water, at the temperature of 50°, takes up 670 times its volume of ammonia (780, THOMSON); its bulk is increased (6 measures of water giving 10 of the solution,) and its specific gravity diminished; that of a saturated solution is 0·875, water being 1·000. The following table shows the quantity of ammonia in solutions of different specific gravities. (DAVY, *Chem. Phil.*, p. 268.)

100 parts of Sp. Gr.		Of Ammonia.	100 parts of Sp. Gr.		Of Ammonia.
8750	contain	32·50	9435	contain	14·53
8875	„	29·25	9476	„	13·46
9000	„	26·00	9513	„	12·40
9054	„	25·37	9545	„	11·56
9166	„	22·07	9573	„	10·82
9255	„	19·54	9597	„	10·17
9326	„	17·52	9619	„	9·60
9385	„	15·88	9692	„	9·50

According to Dalton (*New System of Chem.*, ii. 422,) the following are the strengths of solutions of ammonia of different specific gravities, as also their respective boiling-points:—

Specific Gravity.		Grains of Ammonia in 100 grains of the liquid.		Boiling- Points.		Volumes of gas in one volume of liquid.
·850	35·3	26°	494
·860	32·6	38	456
·870	29·9	50	419
·880	27·3	62	382
·890	24·7	74	346
·900	22·2	86	311
·910	19·8	98	277
·920	17·4	110	244
·930	15·1	122	211
·940	12·8	134	180
·950	10·5	146	147
·960	8·3	158	116
·970	6·2	173	87
·980	4·1	187	57
·990	2·0	196	28

The usual state in which ammonia is employed is in aqueous solution, both in chemistry and medicine. This solution bears the name of *Liquor Ammoniac* in the *London Pharmacopœia*. It may be obtained by passing the gas into water in a proper apparatus; or by distilling over the water and gas together. Dr. Turner recommends for this process, the use of equal parts of sal-ammoniac and well-burned quicklime: the lime is slaked by the addition of water, and as soon as it has fallen into powder, placed in an earthen pan, and covered, till quite cold, then mixed with the powdered sal-ammoniac and put into a proper retort and heated as long as it gives out gas, which should be conducted by means of a safety-

tube of Welter into a quantity of distilled water, equal to the weight of the salt employed. The specific gravity of the solution of ammonia so obtained is .936. (*Elem. of Chem.*, 5th ed., 384.)

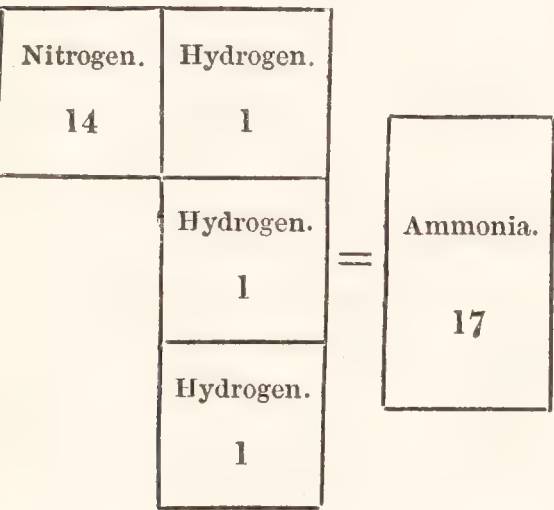
The following process is recommended by Mr. R. Phillips. On 9 ounces of well-burned lime pour half a pint of water, and when it has remained in a well-closed vessel for about half an hour, add 12 ounces of hydrochlorate of ammonia in powder and three pints and a half of boiling water; when the mixture has cooled, pour off the clear portion, and distil from a retort 20 fluid ounces. The specific gravity of this solution, which is sufficiently strong for most purposes, is 0.954. (*Remarks on London Pharmacopœia*, p. 34.) The specific gravity of the officinal solution (*liquor ammoniæ*), directed in the *Pharmacopœia*, is 0.960, and is composed very nearly of 10 grains of ammonia and 90 of water. A cubic inch weighs 242.36 grains, and contains 132 cubic inches of ammoniacal gas. The sp. gr. of the *liquor ammoniæ fortior* (included in the *Materia Medica* of the *Pharmacopœia*) is .882, a cubic inch weighing 222.66 grains, and holding nearly 400 cubic inches of ammoniacal gas. (R. PHILLIPS.)

Liquid ammonia (as this aqueous solution is commonly called) should be preserved in well-stopped glass bottles, since it loses ammonia and absorbs carbonic acid, when exposed to air. When heated, ammonia is rapidly given off by it; when concentrated, it requires to be cooled to -40° before it congeals, and then it is apparently inodorous, and of a gelatinous appearance. If a piece of ice be introduced into a jar of ammonia standing over mercury, it melts with great rapidity, and liquid ammonia is produced.

A pure and strong solution of ammonia is a bad conductor of electricity, but it becomes a conductor when sulphate of ammonia is dissolved in it, and then, if submitted to electrolytic action, Faraday found that nitrogen was evolved at the anode, and hydrogen at the cathode, the ratio of the volume of the former to that of the latter varying, but being as 1 to about 3 or 4. This result seemed to indicate that the electric current had decomposed the ammonia, and that the nitrogen had been determined towards the positive electrode. But when the electricity used was measured out by the voltameter, it was found that the hydrogen obtained was exactly in the proportion which would have been supplied by decomposed *water*, whilst the nitrogen had no certain or constant relation whatever; and upon further experiment, that the water only was electrolyzed, and that the nitrogen at the anode was a secondary result, depending upon the chemical action of the nascent oxygen (determined to that surface by the electric current) upon the ammonia. No experiment has hitherto shown any tendency of nitrogen under the influence of the electric current to pass in either direction along its course. (*Phil. Trans.*, 1834, p. 95.) See *Nitrate of Ammonia*.

Dr. Henry (*Phil. Trans.*, 1809) first observed that a mixture of ammonia and oxygen might be fired by an electric spark, and this property furnishes a means of analyzing the alkaline gas. Electricity also decomposes ammoniacal gas. If a succession of electrical sparks be passed through a small portion of the gas confined in a proper tube over quicksilver, it will increase to about twice its original bulk, and lose its easy solubility in water. If the gas thus expanded be mixed with from

one-third to one-half of its bulk of oxygen, and an electric spark passed through the mixture, an explosion takes place, attended by considerable diminution. Note the amount of the diminution, divide it by 3, and multiply the product by 2. The result shows the quantity of hydrogen; for 2 measures of hydrogen are saturated by 1 of oxygen. Thus, suppose 10 measures of ammonia, expanded by electricity to 18, and that, after adding 8 measures of oxygen gas, we find the whole (= 26 measures) reduced by firing to 6 measures, the diminution will be 20. Then $20 \div 3 = 6.66$; and $6.66 \times 2 = 13.32$ measures of hydrogen gas from 10 of ammonia; and $18 - 13.32 = 4.68$, for the nitrogen gas contained in the product of electrization. Therefore, 10 measures of ammonia have been destroyed and expanded into 13.32 measures of hydrogen and 4.68 of nitrogen gas. (HENRY'S *Elements*, 7th ed., vol. i. p. 233.)



It appears from the above, and from the prior experiments of Berthollet, that 1 volume of ammonia is resolved by decomposition into 2 volumes of a mixture of hydrogen and nitrogen, consisting of 3 volumes of hydrogen and 1 volume of nitrogen; hence the annexed diagrams will represent the composition and volume of ammonia. The results of its detonation with oxygen vary with the quantities of the respective gases: it is obvious that, as far as the combustion

of the hydrogen is concerned, 2 volumes of ammonia (including 3 of hydrogen) will require 1.5 of oxygen; where excess of oxygen is used, more or less nitrate of ammonia is the result of their rapid combustion.

Such being the volumes of the gases, it follows that if we add the specific gravity of nitrogen to thrice the specific gravity of hydrogen and divide the product by 2, we ought to obtain the specific gravity of ammonia;

Specific gravity of nitrogen

=0.971

„ hydrogen

$0.0694 \times 3 = 0.208$

$1.179 \div 2 = 0.589$

Or,

50 cubic inches of nitrogen weigh	15.08
150 „ hydrogen	3.19
<hr/>	
100 „ ammonia	18.27

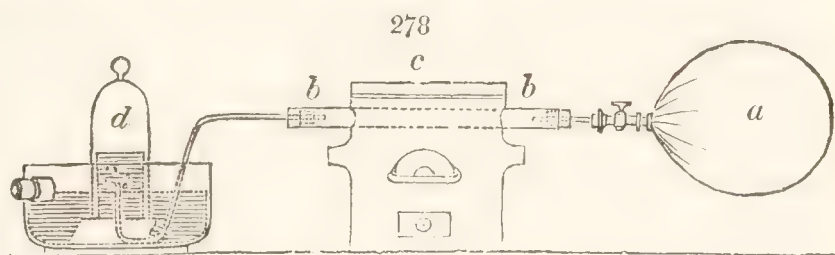
Ammonia, therefore, is a compound of

					Berthollet.	Vols.	Sp. Gr.	100 Cub. In. Grs.	
Nitrogen	1	14	82.35	82.35	1	0.972	30.16
Hydrogen	3	3	17.65	17.65	3	0.208	6.40
<hr/>					<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Ammonia	1		17		100.00	100.00	2	0.590	18.28

When ammonia is detonated with excess of oxygen, a portion of nitric acid seems always to be formed: indeed, according to Bischof, this acid is more or less formed in all cases of its combustion with oxygen. He found the limits of combustibility with oxygen to be on the

one hand, 1 ammonia and 0·6 oxygen; and, on the other, 1 and 3·17 by volume.

When gaseous ammonia is slowly passed through a red-hot porcelain tube filled with fragments of porcelain, so as greatly to increase the surface, more or less of it is decomposed: when passed over an ignited coil of iron or copper wire, the metals become brittle with scarcely a perceptible increase of weight, and the gas is more perfectly decomposed. According to Thenard (*Ann. de Chim.*, LXXV. 61), when any of the five following metals are inclosed in the tube, they promote the decomposition of ammonia at a temperature below that which it requires *per se*, in the following order: iron, copper, silver, gold, platinum. In all these cases the gas suffers expansion, and is resolved into hydrogen and nitrogen gases, in the above stated proportions. (*a* is a bladder filled with ammonia, which may be passed through the iron tube *b* containing wire or turnings of iron or of copper, placed in the furnace *c*; the gas is decomposed, and hydrogen and nitrogen may be collected over the water in *d*.)



Ammonia is also decomposed when passed over black oxide of manganese, heated red-hot in a porcelain tube; the results, which are *water* and *nitrous acid*, were first observed by the Rev. J. Milner. (*Phil. Trans.*, vol. LXXIX.) *Nitrate of ammonia* is also often formed. Passed through a porcelain tube containing red-hot charcoal, ammonia forms a portion of hydrocyanic acid, and nitrogen is evolved. Under similar circumstances the vapor of phosphorus and ammonia yield phosphuretted hydrogen and nitrogen; and with sulphur, sulphuretted hydrogen and hydrosulphuret of ammonia are the results.

Ammonia is produced synthetically during the decomposition of many animal substances; it is also formed during the action of nitric acid upon phosphorus and some of the metals; and by moistened iron-filings exposed to an atmosphere of nitrogen: in these cases the nascent gases unite so as to form a portion of ammonia. When nitric acid is added to a mixture of zinc and dilute sulphuric acid, its nitrogen combines with the evolving hydrogen and ammonia is formed: when, however, the action is violent, some nitric oxide is also evolved. Rust of iron formed by the exposure of iron to a damp atmosphere, generally contains traces of ammonia; but this appears merely to result from its absorption by that substance from the atmosphere, in which ammonia is always present, though in such minute quantities at any one time, as to escape observation, excepting when substances capable of absorbing or condensing it, are present: thus it is that charcoal, humus, clays, and other porous bodies, after exposure to air, yield evidence of ammonia, and that it is traced in rain-water. The importance of this atmospheric ammonia as a source of nitrogen in plants, will be afterwards noticed.

According to Dr. Hare, ammonia is synthetically formed by the action of spongy platinum on a mixture of 2 volumes of nitric oxide and 5 of hydrogen. For such experiments he recommends platinated asbestos

formed by dipping that substance into a solution of chloride of platinum, and exposing it to a red-heat. Some anomalous cases of the evolution and apparent production of ammonia, have been enumerated and commented upon by Faraday, in a paper published in the *Quart. Journ.* (vol. xix. p. 16.)

Ammonia combines with the acids, and produces a class of salts which, with very few exceptions, are readily soluble in water, and which evolve the odor of ammonia when mixed with lime or potassa. These salts are, for the most part, entirely dissipated, and, generally speaking, decomposed by heat. Though at first neutral, most of them become acid by mere exposure to air. (Dr. B. JONES, *Mem. Ch. Soc.*, II. 244.) Ammonia mixed with the gaseous acids condenses them into white pulverulent compounds; it combines either with half its volume, or with an equal volume, or with two volumes of the acid. The same combination ensues when the volatile acids are brought near free ammonia; and in this way very minute quantities of ammonia may be discovered, by dipping a glass rod into hydrochloric, nitric, or acetic acid, and bringing it near any liquid or substance suspected to evolve ammonia, which will be immediately recognised by white fumes. The constitution of ammoniacal salts involves many important theoretical considerations respecting the nature of ammonia, which will presently be adverted to.

AMMONIA AND CHLORINE. When these gases are mixed, a partial decomposition of the former ensues. On mixing 15 parts of chlorine and 40 of ammonia, 5 parts of nitrogen are liberated, and *hydrochlorate of ammonia* is formed. If the gases be dry, considerable heat is evolved, and a flame is perceived to traverse the vessel in which the experiment is made. This combustion of ammonia in chlorine is well shown by annexing to the beak of a small tubulated retort, containing a mixture of hydrochlorate of ammonia and lime, a bent tube, not too small, the extremity of which terminates in a bottle of chlorine; on heating the contents of the retort, ammonia is evolved, and as it issues from the tube into the chlorine, it inflames, and continues to burn with a pale flame, producing hydrochlorate of ammonia, and evolving nitrogen. Dr. Thomson employed *chloride of lime* to decompose ammonia, by mixing it with hydrochlorate of ammonia, and collecting the evolved nitrogen. When solutions of chlorine and ammonia are mixed, an effervescence ensues, nitrogen gas is evolved, and hydrochlorate of ammonia formed; and when gaseous chlorine is transmitted in successive bubbles into a strong solution of ammonia, each produces a slight explosion attended by a flash of light.

The best mode of showing the mutual action of ammonia and chlorine in solution, is to pour into a tube, about two feet long and half an inch in diameter, sealed at one end, a strong aqueous solution of chlorine, to within about two inches of the top; then gradually to pour upon it liquid ammonia, so as to fill the tube, which is to be closed by the thumb, and inverted into water; the solution of ammonia then rises through that of chlorine, and is decomposed with effervescence, nitrogen being evolved, and hydrochlorate of ammonia retained in solution.

CHLORATE OF AMMONIA, $\text{NH}_3\text{ClO}_5\text{HO}$, is formed by saturating chloric acid with carbonate of ammonia. It forms very soluble acicular crystals, of a sharp taste, which detonate when thrown upon hot coals. (VAUQUELIN, *Ann. de Ch.*, xcv. 97.)

Wonfor prepared this salt by adding a saturated boiling solution of chlorate of potassa to a similar solution of bitartrate of ammonia, the liquor being strained from the precipitated bitartrate of potassa as rapidly as possible, since the ammoniacal salt undergoes a change if allowed to remain at a high temperature: the solution was then evaporated at below 100° , and again strained to separate a little tartar: the chlorate of ammonia crystallizes either in small acicular prisms, or in plates like chlorate of potassa, soluble in water and alcohol, and of a sharp, cooling taste: its formula may be assumed as $= \text{NH}_4\text{O}, \text{ClO}_5$. When this salt had been kept a few days, it became yellow, acquired an irritating odor, and having been set aside, the bottle which contained it was found shattered in pieces: another sample of the salt exploded spontaneously in the same way, and broke a strong phial; it appears probable that these dangerous explosions arise from the gradual formation of chloride of nitrogen. (*Phil. Mag.*, July, 1843.)

PERCHLORATE OF AMMONIA, $\text{NH}_3, \text{ClO}_7, \text{HO}$, crystallises in prisms, soluble in 5 parts of cold water, and sparingly soluble in alcohol. (SERULLAS, *Ann. Ch. et Ph.*, xlvii., 304.)

AMMONIA AND HYDROCHLORIC ACID. HYDROCHLORATE OF AMMONIA. MURIATE OF AMMONIA. SAL-AMMONIAC. NH_3, HCl . CHLORIDE OF AMMONIUM. NH_4, Cl . This salt may be produced, directly, by mixing equal volumes of gaseous ammonia and hydrochloric acid, when entire condensation ensues. Under the name of *sal-ammoniac* this salt was formerly imported from Egypt, where it was obtained by burning the dung of camels (PARKES'S *Essays*, ii. 437); it is now prepared either by saturating carbonate of ammonia by hydrochloric acid, or by decomposing sulphate of ammonia by chloride of sodium. ($\text{NH}_3, \text{SO}_3, \text{HO} + \text{NaCl} = \text{NH}_3, \text{HCl} + \text{NaO}, \text{SO}_3$.) When obtained by evaporation from its solution in water, it forms octohedral, cubic, and plumose crystals; but, in commerce, it usually occurs, as procured by sublimation, in colorless and translucent cakes, hard, and somewhat elastic, specific gravity 1.45 to 1.50, and very slightly deliquescent: in this compact state it requires for solution about an equal weight of water at 212° , and nearly three times its weight at 60° , cold being produced during its solution; it also dissolves sparingly in alcohol: when heated it sublimes before it fuses, without decomposition, in the form of white vapor, and may be even passed through a red-hot porcelain tube without change. Heated with potassium it yields chloride of potassium, 1 volume of hydrogen and 2 of ammonia being evolved: ($\text{NH}_4, \text{Cl} + \text{K} = \text{KCl} + \text{NH}_3 + \text{H}$; or $\text{NH}_3, \text{HCl} + \text{K} = \text{KCl} + \text{NH}_3 + \text{H}$.) It is also decomposed when transmitted over ignited iron or copper wire. The specific gravity of its vapor is 0.92.

						Bucholz.	Berzelius.		
Ammonia	1	...	17	...	31.48	...	31	...	31.95
Hydrochloric acid	1	...	37	...	68.52	...	69	...	68.05
<hr/>									
Hydrochlorate of ammonia	1		54		100.00		100		100.00
<hr/>									
			Volumes.				Sp. Grav.		
Ammoniacal gas.....			0.5			0.295		
Hydrochloric acid gas			0.5			0.630		
<hr/>									
			1.0				0.925		

Sal-ammoniac is not volatile at common temperatures, but when its aqueous solution is boiled, traces of the salt pass off with the vapor of the water; when exposed to air it becomes slightly acid in consequence of the loss of a little ammonia; the aqueous solution, therefore, of the salt, often reddens litmus: it is used in the arts for a variety of purposes, especially in certain metallurgic operations; it is used in tinning, to prevent the oxidation of the surface of copper; it is also employed in small quantities by dyers. Dissolved in nitric acid, it forms the *Aqua Regia* of commerce, used for dissolving gold, instead of the mixture of nitric and hydrochloric acids. It is employed, dissolved in small quantities in the water, to prevent calcareous deposits in steam-boilers. (*See Salts of Lime.*)

Native sal-ammoniac occurs massive and crystallized, in the vicinity of volcanoes, and in the cracks and pores of lava near their craters. It has thus been found at Etna and Vesuvius, in the Solfaterra near Naples, and in some of the Tuscan lakes. An efflorescence of it is sometimes seen upon pit-coal. Its color varies, from the admixture of foreign matter, and it is frequently yellow from the presence of sulphur. It is said that considerable quantities of native sal-ammoniac are also found in Bucharica, where it occurs with sulphur in rocks of indurated clay. The ancients, according to Pliny, called this salt *ammoniac*, because it was found near the temple of Jupiter Ammon, in Africa. It has been detected by Dr. Marcet in sea-water. (*Phil. Trans.*, 1822, p. 454.)

AMMONIA AND IODINE. Iodine absorbs dry ammoniacal gas, and produces a viscid compound, at first of a metallic appearance, but becoming deep brown and more liquid by excess of ammonia. Added to water, it produces a crimson-colored solution, and yields iodide of nitrogen: it is also soluble in alcohol, and acts more powerfully on organic matter than pure iodine. Exposed to air, it ultimately leaves a pale-brown powder, powerfully detonating, and exhibiting a bright light at the moment of explosion. Landgrebe, who has ascertained these facts (*Poggend. Ann.*, xiv., 539), considers this as a distinct iodide of nitrogen. It detonates at the temperature of about 80° . The action of iodine on liquid ammonia has been already described. Berzelius regards the iodide of ammonia as an hydriodate of iodide of nitrogen and of ammonia. Bineau states that 100 parts of iodine absorb 20.4 of ammonia, which is in the proportion of 2 atoms of iodine and 3 atoms of ammonia. (*Ann. Ch. et Ph.*, Lxvii. 228.)

IODATE OF AMMONIA, $\text{NH}_3, \text{IO}_5, \text{HO}$, is obtained by saturating iodic acid with ammonia. It forms small crystals, sparingly soluble in water; it deflagrates, when thrown upon hot coals, with a pale violet flame; heated highly in a tube it explodes, and is decomposed into oxygen, nitrogen, water, and iodine. Its composition has not been experimentally ascertained, but it contains, according to Rammelsberg, 85.9 per cent. of iodic acid (*Poggend.*, XLiv. 555), the probable constitution, therefore, of the salt, is

Ammonia.....	1	17	8.86
Iodic acid.....	1	166	86.46
Water	1	9	4.68
<hr/>					
Iodate of ammonia	1		192		100.00

HYDRIODATE OF AMMONIA. IODIDE OF AMMONIUM. NH_3, HI , or NH_4I . In a former paragraph the action of iodine on aqueous ammonia has been stated to produce a portion of hydriodate of ammonia; this compound may be directly formed by mixing equal volumes of hydriodic and ammoniacal gases; or by saturating liquid hydriodic acid by carbonate of ammonia: it forms very soluble and deliquescent cubic crystals, which are anhydrous, and volatile in close vessels without decomposition. Its aqueous solution dissolves iodine. (GAY LUSSAC, *Ann. Chim.*, xci.) Hydriodate of ammonia consists of

Ammonia	1	17	11.81
Hydriodic acid	1	127	88.19
<hr/>					
Hydriodate of ammonia	1		144		100.00

AMMONIA AND BROMINE act on each other with the evolution of nitrogen, and form *hydrobromate of ammonia*; but no *bromide of nitrogen*.

BROMATE OF AMMONIA, $\text{NH}_3, \text{BrO}_5, \text{HO}$, obtained by saturating ammonia by bromic acid, yields acicular and granular crystals of a pungent, cooling taste, subject to explosive decomposition. (RAMMELSBERG, *Poggend.*, lii. 85.)

HYDROBROMATE OF AMMONIA. BROMIDE OF AMMONIUM, NH_3, HBr or NH_4Br . This is a volatile prismatic salt, becoming yellow and slightly acid by exposure to air. It is constituted of equal volumes of gaseous hydrobromic acid and ammonia. It is very soluble in water, and sparingly soluble in alcohol. (BALARD.)

HYDROFLUATE OF AMMONIA. FLUORIDE OF AMMONIUM. NH_3, HF , or NH_4F . According to Berzelius, the neutral hydrofluat is best obtained by heating in a platinum crucible a mixture of 1 part of hydrochlorate of ammonia with 2.25 parts of fluoride of sodium, both in fine powder: the cover of the crucible should be inverted, and contain water, to be replaced as it evaporates, so as to prevent its temperature exceeding 212° . A gentle heat sublimes the salt, which attaches itself in small prismatic crystals to the cool cover. If the salts are moist, ammonia is evolved, and an acid salt obtained. *Hydrofluat of ammonia* is permanent in the air, readily soluble in water, and less so in alcohol. At a high temperature it melts before it sublimes; it corrodes glass, and its solution furnishes a ready means of etching upon it; it absorbs ammonia, but does not retain it when sublimed. When its solution is evaporated, ammonia gradually escapes, and a remarkably deliquescent *bihydrofluat of ammonia*, imperfectly crystallizable, remains.

HYPONITRITE OF AMMONIA, $\text{NH}_3, \text{NO}_3, \text{HO}$, is obtained when neutral hyponitrite of lead is decomposed by sulphate of ammonia. Its solution is decomposed by a very gentle heat, and evolves nitrogen, but it remains neutral. Exposed to spontaneous evaporation in a dry atmosphere, an irregularly crystallized mass is obtained, which melts, and is decomposed when heated, being resolved into nitrous oxide, water, and ammonia. (BERZELIUS.)

NITRATE OF AMMONIA. $\text{NH}_3, \text{NO}_5, \text{HO}$; or $\text{NH}_4\text{O}, \text{NO}_5$. This salt may be formed by the direct union of ammonia with nitric acid. It is

usually obtained by saturating pure nitric acid with carbonate of ammonia, evaporating, and crystallising. It has been mentioned as the source of *nitrous oxide*, and when carefully heated it is entirely resolved into that gas and water. $\text{NH}_4\text{O}, \text{NO}_5 = 2 \text{NO} + 4 \text{HO}$.

Nitrate of ammonia was formerly called *Nitrum flammans*, in consequence of its rapid decomposition with a slight explosion when heated to about 600° . At 228° it enters into perfect fusion; at 356° it boils without decomposition: at about 390° to 400° , it is decomposed. It differs in form according to the manner in which its solution has been evaporated; if at a temperature below 100° , its crystals are six-sided prisms terminated by six-sided pyramids; if boiled down, its crystals are thin and fibrous; its sp. gr. is 1.7. It is deliquescent, and soluble in less than its weight of water at 60° . Its taste is acrid and bitter. It indicates free acid after exposure to air, and, like other ammoniacal salts, it loses its neutrality when its solution is boiled. According to Berzelius, the *prismatic* variety affords 11.232 *per cent.* of water: hence it may be considered as containing

						Berzelius.		Ure.
Ammonia.....	1	17	21.25	21.143 23.3
Nitric acid	1	54	67.50	67.625 65.0
Water	1	9	11.25	11.232 11.7
<hr/>			<hr/>			<hr/>		
Prismatic nitrate of ammonia	1		80		100.00		100.000	100.0

According to Dumas, the salt always includes 2 atoms of water.

AMIDOGEN. NH_2 . **AMMONIUM.** NH_4 . Neither of these compounds have been isolated. Amidogen is presumed to exist in combination with certain metals, and in some organic compounds. When potassium, or sodium, for instance, is heated in ammonia, 1 equivalent of hydrogen is evolved, and a compound $= \text{M}, \text{NH}_2$ remains (see *Potassiamide*); and one of the results of the decomposition of oxalate of ammonia by heat is a white substance called *Oxalamide*, $= \text{C}_2\text{O}_2 + \text{NH}_2$. Inferring from these and other similar cases, that in ammonia the third atom of hydrogen is less intimately combined with nitrogen than the remaining two, Dr. Kane represents amidogen, $\text{NH}_2 = \text{Ad}$, as the radical of ammonia, and ammonia, therefore, as an *amidide of hydrogen* $= \text{NH}_2, \text{H}$ or AdH .

AMMONIUM. When a globule of mercury is made the negative electrode in an aqueous solution of ammonia, it becomes semifluid, and assumes the character of a soft amalgam; oxygen is given off at the positive electrode, but there is no corresponding evolution of hydrogen on the negative side till the electric current is interrupted, when the metallic sponge begins to collapse, and giving out hydrogen and ammonia, a mere globule of mercury ultimately remains; but this change may be retarded by cold, and on cooling the pasty mass to 0° it yields cubic crystals, which, when decomposed over mercury, give out ammonia and hydrogen in the respective volumes of 2 to 1. The mercury, therefore, appears to have been combined with a body represented by NH_4 , and as the metallic characters of the mercury are not impaired, it is presumed that NH_4 constitutes a body having the characters of a metal, which has therefore been termed *ammonium*. The same phenomenon may be observed by adding a minute quantity of potassium to mercury, and placing the alloy upon a piece of sal ammoniac moistened with ammonia or a solution of

the salt; it soon puffs up, and assumes the characters of the amalgam: it is supposed in this case that the potassium alloy acting upon hydrochlorate of ammonia, gives rise to chloride of potassium, and the ammonium alloy: $KHg + NH_3HCl = KCl + HgNH_4$. If upon these data we admit the existence of *ammonium*, (that is, of a body having the properties of a metal and composed of 1 atom of nitrogen and 4 of hydrogen, NH_4 ,) the ammoniacal salts will then be perfectly assimilated to those of the other metallic oxides, and may be represented as constituted of an atom of *oxide of ammonium* combined with the respective acids, and the necessity of the atom of water to the constitution of these salts becomes apparent. Thus, instead of representing nitrate of ammonia as containing 1 equivalent of ammonia, 1 of nitric acid, and 1 of water $= NH_3, NO_5, HO$, it will become a *nitrate of oxide of ammonium* $= NH_4O, NO_5$. And instead of considering sal ammoniac as a hydrochlorate of ammonia $= NH_3, HCl$, it will become assimilated to the other metallic chlorides, and be represented as a chloride of ammonium, $= NH_4, Cl$. An important fact in favour of the ammonium theory presents itself in the phenomena of the electrolysis of ammoniacal salts: when nitrate of ammonia is thus decomposed, NH_4 is evolved at the negative pole, and NO_6 (Daniell's *Oxynitron*) at the positive pole; with oxalate of ammonia NH_4 appears at the negative, and C_2O_4 at the positive; and so on*. It was well remarked by Professor Daniell, that, although there is something startling to our preconceived notions in supposing that a permanent gas or a combination of permanent gases, should present itself as a metal, there are yet analogies in favor of such a view, for in many chemical combinations hydrogen may be substituted for metals, and hydrogen is the only elementary substance which, in cases of electro-decomposition, follows the same course as the metals; and, again, "hydrogen differs in nothing from mercury in a state of vapor except its density, and the lowness of its point of vaporisation. The vapor of mercury at its boiling-point has none of those characters which we are apt to suppose ought predominantly to distinguish a metal; it is perfectly transparent and colorless, and moreover, it is a perfect non-conductor of electricity." (*Introduction to Chemical Philosophy*, § 704.)

In reference, therefore, to this, which has been termed the "ammonium theory," the combinations of ammonia with the oxyacids and with the hydracids, instead of standing out as anomalous exceptions to the usual constitution of salts, become assimilated to the whole series; and

* In the decomposition above alluded to, in which it is assumed that the electrolysis of nitrate of ammonia yields NO_6 (or *oxynitron*) and NH_4 (or *ammonium*) at the positive and negative electrodes, it is evident that the products actually found there are not NO_6 and NH_4 , but $NO_5 + O$ and $NH_3 + H$, and it is generally supposed that the ions which actually travel in the circuit, are nitric acid and oxygen, and ammonia and hydrogen; that is, that the proximate elements of the salt appear at the poles, along with the ultimate elements of the water: the solution of this problem is of great importance in reference to the

theory of electrolytic action as well as to that of the constitution of acids and salts. Daniell and Miller (*Phil. Trans.*, 1839, 1840, and 1844), seem to suspect that the water itself is not decomposed, that it is not, in fact, an electrolyte, but that the true ions are NO_6 and NH_4 , and that inasmuch as these cannot exist in the isolated state, NO_6 on its separation becomes $NO_5 + O$, and that NH_4 becomes $NH_3 + H$, so that nitric acid and ammonia remain in the water, while oxygen and hydrogen are evolved as gases. Applications of these views to other compounds will appear in the sequel.

upon this view the isomorphism of the ammonium and potassium salts is easily explained: thus, if we represent NH_4 , by Am, we have the corresponding series as follows:—

	Potassium Series.		Ammonium Series.
Metal	K	Am	= NH_4
Oxide	KO	AmO	= NH_4O
Chloride	KCl	AmCl	= NH_4Cl
Nitrate	KO, NO_5	AmO, NO_5	= $\text{NH}_4\text{O}, \text{NO}_5$.

ATMOSPHERIC AIR.

THE composition of the *atmosphere* has been frequently alluded to in the preceding pages, and now that we are acquainted with its essential elements, nitrogen and oxygen, it will be useful to consider its nature and properties somewhat more in detail.

The atmosphere is a thin, transparent, invisible, and elastic fluid, which surrounds and revolves with our planet, and reaches to a considerable height above its surface, probably between forty and fifty miles. (WOLLASTON. *Phil. Trans.*, 1822.)

That air is a *ponderous* body, was first suspected by Galileo, who found that a copper ball, in which the air had been condensed, weighed heavier than when the air was in its ordinary state of tension. The fact was afterwards demonstrated by Torricelli, whose attention was drawn to the subject by the attempt of a well-digger at Florence to raise water by a common pump to a height exceeding 33 feet. It was then found that the *pressure of the atmosphere*, and not Nature's abhorrence of a vacuum, was the cause of the ascent of the water in the pump-pipe, and that a column of about the height mentioned, was sufficient to equipoise the atmosphere, which, at the level of the sea, presses with a weight of about *fifteen pounds on every square inch of surface*, and is capable of supporting a column of water about 34 feet high. Comparing the specific gravity of mercury with that of air and water, Torricelli inferred that if a column of air one inch square and as high as the atmosphere, weighed 15 pounds, and a column of water 34 feet high and an inch square, weighed also 15 pounds, the height of a similar column of mercury would be about 30 inches, the density of mercury to that of water being as 13.5 to 1. He accordingly, in 1643, filled a glass tube, three feet long, and closed at one end, with mercury, and inverted it in a basin of the same fluid; he found that the mercury fell about six inches, so that the atmosphere did counterbalance a column of *mercury* of about 30 inches in height. The empty space, in the upper part of the tube, has hence been called the *Torricellian vacuum*, and is nearly the most perfect that can be formed. Paschal and Torricelli afterwards observed that, upon ascending a mountain, the mercury fell in the tube, because there was less air above to press upon the surface of the metal in the basin; and thus a method of measuring the heights of mountains by the *barometer*, as the instrument is now called, was devised. Sir Henry Englefield constructed a barometer expressly for these investigations. (*Journal of Science and the Arts*, vol. v., p. 229.) Such instruments are now commonly called *Mountain Barometers*.

The barometer indicates, by its rise and fall, a corresponding change in the pressure of the atmosphere. At the surface of the earth the *mean* density or pressure is considered equal to the support of a column of

mercury 30 inches high, which would give a pressure upon every square inch of about 15 lbs.*

		Inches.
At 1000 feet above the surface the column falls to		28·91
2000	„	27·86
3000	„	26·85
4000	„	25·87
5000	„	24·93
1 mile	„	24·67
2	„	20·29
3	„	16·68
4	„	13·72
5	„	11·28
10	„	4·24
15	„	1·60
20	„	0·95

At a height of 2·705 miles, = 11,556 feet, one volume of the atmosphere would expand into two, its calculated density being diminished at that height by one-half; the density is again halved at every 2·7 miles additional elevation, as in the following table:

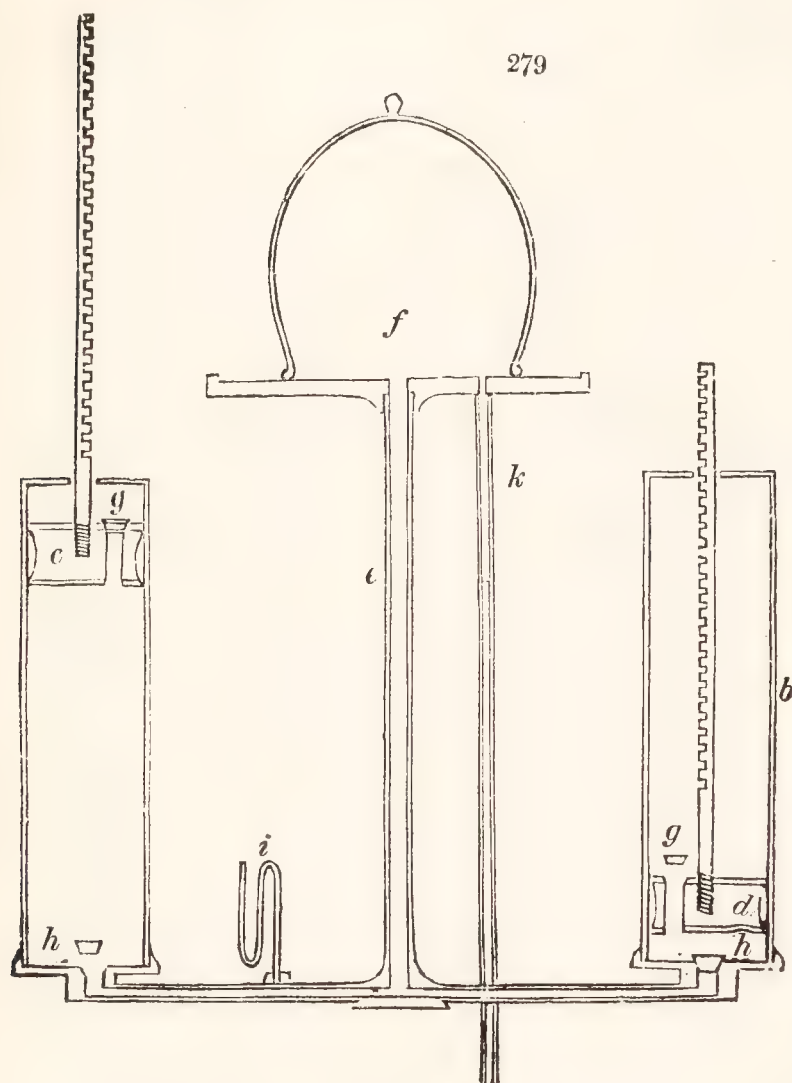
Height above the sea in miles.	Volume.	Height above the sea in miles.	Volume.
0	1	10·820	16
2·705	2	13·525	32
5·410	4	16·230	64
8·115	8	18·935	128

The temperature of the atmosphere diminishes about 1° for every 350 feet of ascent, the cause of which is partly referable to the increased capacity of air for heat in proportion as its density diminishes, and partly to the circumstance that the atmosphere is chiefly heated by the earth. The line of perpetual congelation gradually ascends from the equator to the poles. At 0° latitude it is stated to be 15200 feet; at 60°, 3818; and at 75°, only 1000 feet.

* This is equal to a column of *water* of between 33 and 34 feet in height, and accordingly, in all ordinary cases, the requisite length of the tube prevents the construction of *water-barometers*, but their great rise and fall, as compared with the mercurial column, and the singular facility with which they fluctuate with atmospheric changes, renders observations with such instruments curious and instructive. A water-barometer was put up, in the year 1832, in the Hall of the Royal Society at Somerset House, under the direction of Mr. Daniell, of which an interesting description will be found in the *Philosophical Transactions* for that year; and in the third edition of his *Meteorological Essays*, published shortly after his sincerely lamented death, some additional particulars are given respecting the re-filling of the instrument, which was accomplished under his superintendence, by Mr. Newman, on the 28th of January, 1845. The water in the cistern had originally been covered by castor oil, but as that had not proved quite effectual in preventing the admission of atmospheric air, a solution of caoutchouc

in naphtha was now substituted for it. It is curious to watch the oscillation of this barometer in very windy weather; the column of water appears to be in a perpetual motion, compared by Mr. Daniell to the slow action of respiration; but the most important result is, that this instrument precedes, by one hour, the mercurial barometer of half an inch bore, as this does the mountain barometer of 0·15 inch bore by the same interval, in their horary oscillations, “showing that while philosophers are disputing about the hours of the maxima and minima, much depends upon the construction of the instrument observed.” The first water-barometer seems to have been constructed by Otto Guericke of Magdeburgh: it consisted of a tube above 30 feet high, terminated by a wider glass tube, hermetically sealed, and containing a toy in the shape of a man: all the lower part of the tube, and the cistern in which it stood, were concealed, and the little image only made its appearance in fine weather: to this whimsical contrivance he gave the name of *semper vivum*, or *Anemoscope*.

THE MECHANICAL PROPERTIES OF THE AIR are best illustrated by the *air-pump*, the construction of which much resembles that of the common water-pump, excepting that all the parts are more accurately and nicely made, the object being to exhaust the air as completely and expeditiously as possible.



The annexed sketch (fig. 279,) will give an idea of the operation of the common air-pump. *a b* are cylinders, into which the sliding pistons *c d* are accurately fitted: *e* is a tube issuing from the bell-glass placed upon a brass plate *f*, and entering the lower part of the cylinders at *h h*, where are *valves* opening upwards. In each piston is also a valve opening upwards at *g g*. The cylinder *a* represents the piston in the act of being drawn up. By elevating the piston *c*, an attempt will be made to form a vacuum underneath it; but a portion of the air, in consequence of its elasticity, will pass out of the bell *f*, along

the tube *e*, and elevating the valve *h*, will fill the space below the piston, the valve *g* being kept closed by the weight of the incumbent atmosphere. In the cylinder *b* the piston is represented in the act of depression, the valve *h* therefore is forced down upon the orifice, which it perfectly closes; and the air, confined between it and the piston, now makes its escape by the piston-valve *g*, which is accordingly open, so that at every stroke of the pump a portion of air is withdrawn from the receiver *f*.

With this air-pump it is obviously impossible to obtain more than an imperfect vacuum in the receiver *f*, for the valves can only act by the elasticity of the remaining air; and, accordingly, if a barometer be placed under the receiver, the mercury will never attain a level in the tube and basin, but will always indicate a degree of pressure, as is shown by the small syphon gauge at *i*; and if a tube three feet long (*k*) have its upper end opening into the receiver, and its lower end plunged into a basin of mercury, the mercury will never rise so high as in the common barometer, where the vacuum above it is more perfect, but will indicate the pressure of a remnant of air in the receiver. The *syphon gauge*, and the *barometer-gauge* as applied at *i* and *k*, are very useful appendages to the air-pump, as showing the degree of exhaustion, and its permanence. For the use of the laboratory the valves of the air-pump should be of metal. There are various improved forms of air-pump less liable to derangement, and giving a more perfect vacuum, descriptions of which will be found in works on pneumatics.

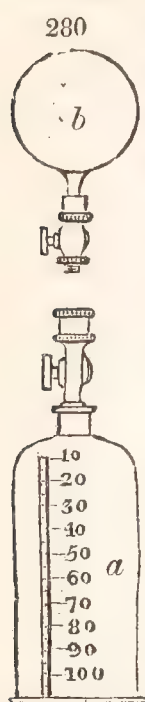
The operation of the pump in removing air, and the mechanical properties of the atmosphere, may be shown by a variety of experiments. Its *pressure* is illustrated by the force with which the bell-glass is pressed down upon the plate of the pump; the *absence of its buoyancy*, by the descent of a guinea and a feather at the same time in the exhausted receiver; and by the preponderance of the larger of two bodies which balance each other in the open air. The *want of resistance* in the exhausted receiver is also shown by the equal duration of the motion of two fly-wheels, with their plates placed in different directions. The *elasticity* of the air is illustrated by the action of the pump itself, or by the distension which a flaccid bladder suffers during the removal of the external air, when placed under the receiver.

The extreme elasticity of the air, and the changes of bulk which it is constantly sustaining under variations of pressure and of temperature, have been already partially adverted to. The general law of its compression was originally developed by Boyle in 1662, and afterwards investigated by Mariotte. They found that the volume of air and all other elastic fluids retaining that state, was inversely as the pressures acting upon them. Thus a volume of air = 100 under any given pressure, will be diminished to 50 when that pressure is doubled; and expanded to 200 when the pressure is diminished by one-half. From the experiments of Oersted (*Edinb. Journal of Science*, iv.), this law applies under very high pressures; indeed, till liquifaction begins to be effected. (See p. 2.) We have, however, no evidence of the liquifaction of atmospheric air under any pressure, Perkins's experiments upon that subject (*Phil. Trans.*) not being conclusive.

SPECIFIC GRAVITY OF AIR. The specific gravity of atmospheric air, at mean temperature and pressure, that is, the thermometer being at 60°, and the barometer at 30 inches, is usually considered as = 1, being the standard of comparison to which the specific gravities of gases and vapors are referred. In consequence of the interfering causes, and the delicacy of the methods required for the determination of the weight of a given bulk of air, the results of different experimentalists are a little at variance; and accordingly the tables of the specific gravities of aëriiform fluids given in different works, are seldom exactly consistent with each other. From the latest experiments of Dr. Prout, 100 cubic inches of pure and dry atmospheric air, at mean temperature and pressure, weigh 31·0117 grains, so that, upon this datum, it is about 815 times lighter than its bulk of water, and 11,065 times lighter than its bulk of mercury. At the temperature of 32°, 100 cubic inches of atmospheric air weigh, according to Dr. Thomson, 32·79 grains. Compared with hydrogen, its specific gravity is as 15·2 to 1. In the following table the weight of 100 cubic inches of the lightest and heaviest known forms of matter are contrasted with air and with water in its different states: their specific gravities compared with air and water are also shown.

100 Cubic Inches.	Weight in grains.	Sp. gr., air being = 1.	Sp. gr., water being = 1.
Hydrogen	2·138	0·0694	0·0000846
Air	31·000	1·0000	0·0012277
Steam	19·220	0·6240	0·0007611
Ice	23735·000	765·0000	0·9400000
Water.....	25250·000	814·0000	1·0000000
Platinum.....	542875·000	17512·0000	21·0000000

DETERMINATION OF THE SPECIFIC GRAVITY OF GASES. For ascertaining the specific gravity of gaseous bodies, a good air-pump is essentially requisite; a light glass balloon (fig. 280) or flask *b*, and a graduated air-jar *a*, each supplied with stop-cocks, are also required. The stop-cock attached to the flask should be as small and light as possible.



Henry (*Elements of Chemistry*), and Faraday (*Chemical Manipulation*), have given explicit directions for determining the specific gravities of gases, of which the following is an abstract.

The gases should be retained and collected over mercury, and carefully dried, by exposing them to proper substances for absorbing the aqueous vapor with which they are mixed, and which would sometimes materially affect the accuracy of the result; or they should be taken saturated with moisture, and a correction afterwards made for the weight of the vapor contained in a given bulk of the gas.

Supposing the receiver *a* to be filled with any gas, the weight of which is to be ascertained, screw the cock of the vessel *b* on the plate of an air-pump, and exhaust it as completely as possible, carefully ascertaining by the barometer gauge of the pump, that it retains its vacuum. The weight of the exhausted vessel is then accurately taken, even to a small fraction of a grain; and it is screwed upon the cock of the receiver *a*. On opening both cocks, the last of which should be turned very gradually, the gas ascends from the vessel *a*; and the volume which enters into the flask is known by the graduated scale on *a*. On weighing the vessel a second time, we ascertain how many grains have been admitted. If we have operated on common air, we shall find its weight to be at the rate of 31 grains to 100 cubical inches. The same quantity of oxygen gas will weigh 34 grains, and of carbonic acid gas 47·3 grains. In these manipulations, care is to be taken not to warm any of the vessels by contact with the hands, from which they should be defended by a glove. On opening the communication between the receiver and the exhausted vessel, if any water be lodged in the air-cock attached to the former, it will be forcibly driven into the latter, and the experiment will be frustrated. This may be avoided by using great care in filling the receiver with water, before passing into it the gas under examination: a small plug of bibulous paper, or of cotton, may also be put into the upper orifice of the stop-cock.

The specific gravity of any gas, compared with common air, is readily known, when we have once determined its absolute weight. Thus, if 100 cubic inches of air weigh 31 grains, and the same quantity of oxygen gas weigh 34 grains, we say,

$$31 : 34 :: 1.000 : 1.1097.$$

The specific gravity of oxygen gas, compared with atmospheric air, will therefore be as 1.097 to 1.000.

We may determine, also, the specific gravity of gases more simply by weighing the flask, first when full of common air, and again when exhausted; and afterwards by admitting into it as much of the gas under examination as it will receive, and weighing it a third time. Now, as the

loss between the first and second weighing is to the gain of weight on admitting the gas, so is common air to the gas whose specific gravity we are estimating. If, for example, by exhausting the flask it loses 31 grains, and by admitting carbonic acid it gains 47·3: then

$$31 : 47·3 :: 1·000 : 1·525.$$

The specific gravity of carbonic acid is, therefore, 1·525, air being taken at 1·000. And knowing its specific gravity, we can, without any further experiment, determine the weight of 100 cubic inches of carbonic acid; for, as the specific gravity of air is to that of carbonic acid, so is 31 to the number required; or

$$1·000 : 1·527 :: 31 : 47·3.$$

100 cubic inches, therefore, of carbonic acid, will weigh 47·3 grains.

In consequence of the facility with which the bulk of aëriiform bodies is altered by variations of pressure and temperature, these must always be taken into account when speaking of their respective volumes; for convenience sake, they are generally therefore reduced to what is termed *mean pressure and temperature*: *mean pressure* being that which sustains 30 inches of mercury in the barometer tube, and *mean temperature* that of 60° of Fahrenheit, or about 15° of the Centigrade scale. This, at least, is the most convenient thermometric point, though it is not always adhered to. By Act of Parliament, the temperature at which the specific gravity of spirituous liquors is determined for the purposes of the excise, and that at which the standard weights and measures are adjusted, is 62°.

The following are the rules for the reduction of gaseous volumes to mean pressure and temperature.

First, in respect to *pressure*, (assuming the mean height of the barometer as = 30 inches,) it is obvious that as the mean height of the barometer is to the observed height, so is the observed volume to the volume required. Suppose, for instance, we had measured 100 cubic inches of air at a barometrical pressure of 29 inches, and wished to know what would be its volume at 30 inches, we shall find by the rule of proportion that

Mean height.	Observed height.	Observed volume.	Required volume.
30	29	100	96·66

Or, in regard to weight, suppose that with the barometer at 29 inches, we had found 100 cubic inches of air to weigh 29·97 grains, and wished to know what the weight would be at standard pressure, we shall find by the rule of proportion that

Observed height.	Mean height.	Observed weight.	Required weight.
29	30	29·97	31

Secondly, in respect of *temperature*, it has been above stated (page 37) that 100 volumes of air at 32° become 137·5 at 212°, the increase being $\frac{37·5}{100}$ th of the original bulk: dividing this by 180, it is found that a volume of air dilates $\frac{1}{480}$ th of the volume which is occupied at 32° for every degree of Fahrenheit's scale, and the same law applies to all other aëriiform bodies not in contact with any liquid. If, therefore, it be required to know what volume 100 cubic inches of air at 70° would occupy at 60°, we must bear in mind that it is not $\frac{1}{480}$ th part per degree of the observed volume at 70° which is to be deducted; but $\frac{1}{480}$ th part of the volume which 100 cubic inches at 70° would occupy at 32°. Now, 480

parts of air at 32° , become 481 parts at 33° , and increase one part for every additional degree, so that at 60° they have increased to 508 parts, and at 70° to 518 parts, and thus we have a proportion between the volumes at 60° and 70° by which we can determine the question: for

Volume at 70° .		Volume at 60° .		Cub. in. at 70° .		Cub. in. at 60° .
480 + 38	:	480 + 28	::	100	:	98.069;

or, on the other hand, if we wish to know the correct volume at 60° , of 40 cubic inches of air observed at 35° ,

Volume at 35° .		Volume at 60° .		Cubic inches.		Cubic inches.
480 + 3	:	480 + 28	::	40	:	42.07.

Again; the weight of 100 cubic inches of air being 31 grains at 60° , the weight of an equal volume at 212° will be found as follows:—

Volume at 212° .		Volume at 60° .		Grains.		Grains.
480 + 180	:	480 + 28	::	31.0	:	23.86

In making the correction for temperature in addition to that for pressure, it matters not which is first applied to the observed volume, as the result will be the same in either case. (DANIELL'S *Introduction*, § 154.)

It has already been observed that gas, when standing over water, becomes saturated with aqueous vapor, the quantity being proportional to the temperature. In such cases a part of the observed volume, as well as of the weight, is due to vapor, which therefore must be determined before the actual weight of the gas can be accurately calculated. The following table (FARADAY, *Manipulation*, 2nd edition, p. 376,) exhibits the proportion by volume of aqueous vapor existing in any gas standing in contact with water at the corresponding temperatures and at mean barometric pressure.

40°	·00933	54°	·01533	68°	·02406
41	·00973	55	·01586	69	·02483
42	·01013	56	·01640	70	·02566
43	·01053	57	·01693	71	·02653
44	·01093	58	·01753	72	·02740
45	·01133	59	·01810	73	·02830
46	·01173	60	·01866	74	·02923
47	·01213	61	·01923	75	·03020
48	·01253	62	·01980	76	·03120
49	·01293	63	·02050	77	·03220
50	·01333	64	·02120	78	·03323
51	·01380	65	·02190	79	·03423
52	·01426	66	·02260	80	·03533
53	·01480	67	·02330		

By reference to this table, which is founded upon the experiments of Dalton and Ure, and includes any temperature at which gases are likely to be weighed, the proportions in bulk of vapor present, and consequently of the dry gas, may be easily ascertained. For this purpose the observed temperature of the gas should be looked for, and opposite to it will be found the proportion in bulk of aqueous vapor at a pressure of 30 inches. The volume to which this amounts should be ascertained and corrected to mean temperature. Then the *whole* volume is to be corrected to mean temperature and pressure, and the corrected volume of vapor subtracted from it. This will leave the corrected volume of dry gas. It has been ascertained, in a manner approaching to perfect accuracy, that a cubic inch of permanent aqueous vapor

corrected to the temperature of 60° , and a mean pressure of 30 inches, weighs 0.1929 grains. The weight, therefore, of the known volume of aqueous vapor is now easily ascertained, and this being subtracted from the weight of the moist gas, will give the weight of the dry gas, the volume of which is also known. As an illustration, suppose a gas standing over water had been thus weighed, and that 220 cubic inches at the temperature of 50° Fahr., and barometric pressure of 29.4 inches, had entered into the globe and caused an increase in weight of 101.69 grains. By reference to the table it will be found that at the temperature of 50° , the proportion of aqueous vapor in gas standing over water is .01333, which in the 220 cubic inches will amount to 2.933 cubic inches, which, corrected to the temperature of 60° , becomes 2.942 cubic inches. The whole volume corrected to mean temperature and pressure will be found to equal 219.929 cubic inches, from which, if the 2.942 cubic inches of aqueous vapor present be subtracted, it will leave 216.987 cubic inches as the volume of *dry* gas at mean temperature and pressure: 2.942 cubic inches of aqueous vapor weigh .5675 grains, for $2.942 \times 0.1929 = 0.5675$; this subtracted from 101.69, the whole weight, leaves 101.1225 grains, which is the weight of the 216.917 cubic inches of dry gas; and by the simple rule of proportion, therefore, it will be found that 100 cubic inches of such gas, when dried, and at mean temperature and pressure, will weigh 46.603 grains.

Daniell (*Introduction*, § 203) gives the following data for calculating the amount of the correction for moisture. "Suppose we found 100 cubic inches of a gas saturated with vapor, properly corrected for the temperature of 60° , and 30 inches pressure, to weigh 31 grains, and wished to know the equivalent bulk and weight of the dry gas. The observed volume is partly due to the expansion occasioned by the vapor, and this portion will be in the same proportion to the whole as the elasticity of the vapor is to the total elasticity: therefore,

Barom. pressure.	Force of vap. at 60° .	Cubic inches.	Cubic inches.
30.000	: 0.560	:: 100	: 1.86.

The volume of the dry gas is therefore $100 - 1.86 = 98.14$ cubic inches. Now this expansion of 1.86 cubic inches may be regarded as so much vapor of the same elasticity as the air diffused through the whole space; and as the specific gravity of such steam compared to air is as 0.620 to 1.000, then

Sp. Gr. of Air.	Sp. Gr. of Steam.	Grains.	Grains.
1	: 0.620	:: 31	: 19.22 = weight of 100 cubic inches of steam;
Cubic inches.	Grains.	Cubic inches.	Grains.
and 100	: 19.22	:: 1.86	: 0.35,

which gives the weight of the vapor to be deducted from the total weight: making the weight of 98.14 cubic inches of dry air $31 - 0.35$, or 30.65.

When it is required to deprive gases of vapor, so as to render them *dry*, they may be slowly passed through a tube about half an inch diameter, and from two to three feet long, containing fragments of fused and

dry chloride of calcium, which, by its strong attraction for moisture, effects the desiccation of the gas. A few gases are, however, absorbed by it, in which case fused potassa, or fused carbonate of potassa, duly comminuted, may be substituted. Some gases are conveniently dried by exposing them to a surface of sulphuric acid. (FARADAY'S *Manipulation*, p. 386.)

COMPOSITION OF THE ATMOSPHERE. Atmospheric air has already been stated to consist essentially of oxygen and nitrogen: these gases are merely in a state of mixture, and not in combination. There are various ways of learning the proportion which the oxygen bears to the nitrogen; and as the relative fitness of the air for breathing has sometimes been considered as depending upon the quantity of oxygen contained in a given volume, the instruments used in these experiments have been called *eudiometers*.

From facts already stated, it is obvious, that if atmospheric air, mixed with a certain quantity of *hydrogen*, be detonated by the electric spark, the absorption will be proportionate to the quantity of oxygen present. When 100 measures of pure hydrogen are mixed with 100 of pure oxygen, the diminution of bulk after detonation will amount to 150 parts; that is, one volume of oxygen condenses two of hydrogen. If we introduce into the graduated detonating tube (fig. 265) 300 measures of common air, and 200 of pure hydrogen, there will remain, after detonation, 314 measures; so that 186 measures will have disappeared, of which one-third may be estimated as pure oxygen: hence 300 parts of air have thus lost 63 of oxygen, or 21 *per cent*.

The general rule, therefore, for thus estimating the amount of oxygen in air may be stated as follows:—Add to 3 measures of the air under examination 2 measures of pure hydrogen; detonate; and, when the vessel has cooled, observe the absorption; divide its amount by 3, and the quotient is the quantity of oxygen. This method was first resorted to by Volta, and is susceptible of great accuracy, since hydrogen is easily procured almost absolutely pure. An improved detonating tube for these purposes has been described by Gay Lussac. (*Ann. Ch. et Ph.*, iv. 188.) The simplest form of instrument, however, for detonating gaseous mixtures, is that contrived by Dr. Ure; it consists of a glass syphon with legs nearly of equal length, open and slightly funnel-shaped at one extremity, and hermetically sealed and supplied with platinum detonating wires at the other. The sealed leg is graduated into 100 equal parts; or into subdivisions of the cubic inch. To use this instrument, it is filled with mercury, and inverted in the pneumatic trough; a convenient quantity of the gaseous mixture is introduced, and having applied a finger to the orifice, the tube is removed and inverted so as to transfer the gas to the sealed leg, where its quantity is very accurately measured; we then pour a portion of mercury from the open end of the tube, so as to leave a space of about two inches, and closing the aperture with the thumb, detonate by the electric spark: the included portion of air serves as a spring, and, on withdrawing the thumb, the change of bulk is read off, having previously added mercury, so as to bring it to a level in both legs of the syphon. Any liquid or solid

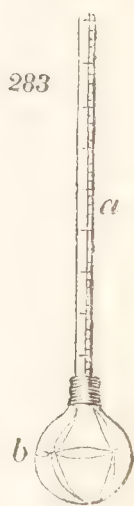
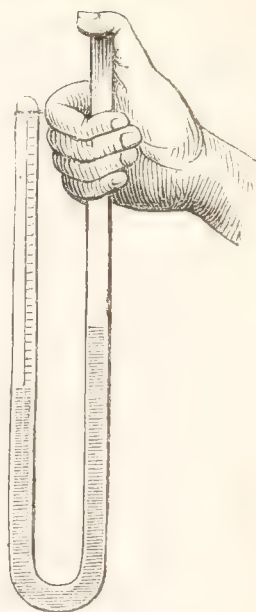
that is required, may then be passed up into the closed end for the analysis of the residuary gas. (*Edin. Phil. Trans.*, 1818.) The annexed cut (fig. 281) represents the mode of holding the tube and firing the included gases.

The action of *spongy platinum*, already mentioned (p. 304,) may be resorted to, to effect the union of oxygen and hydrogen in eudiometrical experiments; or, the air under examination may be mixed with its bulk of pure hydrogen, and two or three of the small balls, composed of spongy platinum and clay, thrown up into the mixture standing over mercury; in the course of an hour or two, when the diminution of bulk has attained its maximum, and the vessel has cooled, the residuary gas is carefully measured, and one-third of its loss of bulk is = to the oxygen. Ure's eudiometer, or a similarly bent tube, may be conveniently used in these experiments, there being no difficulty in conveying one of the platinum pellets into the sealed leg of the tube.

Scheele, in his eudiometrical experiments, employed *sulphuret of potassium*, the solution of which absorbs oxygen, as may be shown by agitating it with atmospheric air in a graduated glass tube. In this experiment the nitrogen remains unaltered. The *eudiometric tubes* of Hope (*NICHOLSON'S Journal*, vol. iv.) and Henry (*Elements*, vol. i. p. 149,) as represented in the marginal wood-cuts (fig. 282 and 283,) are convenient for such experiments by absorption. The former consists of a small bottle, holding about three ounces, into which the graduated glass tube *a* is carefully fitted by grinding. It also has a ground stopper at *b*. To use it, the phial is filled with the solution of the alkaline sulphuret, and the tube *a*, containing the air to be examined, fitted into its place. After inverting and agitating the instrument, the stopper *b* may be opened under water, and the absorption is shown by the rise of the fluid in the tube. For the glass-bottle, Dr. Henry substituted the elastic gum-bottle *b* (fig. 283,) in the neck of which a short piece of glass tube is secured, into which the tube *a* is fitted by grinding. In the *Philosophical Transactions* for 1807, Pepys has described a modification of this eudiometer, which may be often advantageously employed in delicate experiments, and by which an absorption of a thousandth part of the gas under examination may be measured.

When *nitric oxide gas* and atmospheric air are mixed, there is a production of hyponitrous and nitrous acid, in consequence of the union of oxygen with the oxide; and if the mixture be made over water, an absorption proportional to the quantity of acid formed ensues. Upon this principle nitric oxide has been used in eudiometrical experiments; but it does not furnish accurate results. Priestley and Cavendish, (*Phil. Trans.*, 1783,) availed themselves of this mode, and Dalton has offered

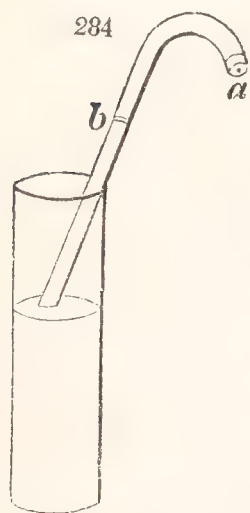
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some remarks upon it. (*Phil. Mag.*, vol. xxviii.) “The most certain results are obtained by adding to 100 parts of the atmospheric air, previously introduced into a small beer-glass, an equal volume of nitric oxide gas; the mixture may be gently agitated, and in two or three minutes carefully decanted into a graduated tube, when it will be found, provided the nitric oxide be pure, that 84 measures have disappeared, of which one-fourth, or 21 measures, are oxygen.”

H. Davy suggested the use of a *solution of protosulphate of iron, impregnated with nitric oxide gas*, for the absorption of oxygen; it may be employed in the same way as the alkaline sulphuret.

If a stick of *phosphorus* be confined in a portion of atmospheric air, it will slowly absorb the oxygen present. The rapid combustion of the



same substance may also be conveniently resorted to.

For this purpose a small piece of phosphorus may be introduced into the bulb of the tube *a* (fig. 284,) containing a given measure of the air to be examined, confined over mercury, which, to prevent loss by expansion, should be suffered to occupy about half the tube, or to stand at *b*. The phosphorus may then be inflamed, and distilled through the air in the tube; and when the combustion is over, and the tube cold, the residuary air may be transferred for measurement. These eudiometrical methods were used by Lavoisier, Berthollet, and Seguin, (*Ann. de Ch.*, ix. and xxxiv.,) and are both sus-

ceptible of accuracy; a loss of volume amounting to between 20 and 21 per cent. of the atmospheric air invariably occurred.

Dupasquier uses the hydrated protoxide of iron as a means of abstracting the oxygen of the air: he has described the mode of applying it in the *Ann. Ch. et Ph.* for October, 1843.

Gay Lussac has recommended the use of slips of copper moistened with hydrochloric acid, for the removal of oxygen from the air. Sausure used thin turnings of clean metallic lead, which when agitated with a little water in the contact of air, absorb its oxygen, and form hydrated oxide of lead. Berzelius employs the liquid amalgam of lead and mercury for the same purpose. Of these various processes, detonation with, or absorption by, hydrogen, and the action of burning phosphorus, are those which are usually resorted to, and are most precise and easily performed.

By experiments thus conducted, it has been found that the composition of the atmosphere is extremely uniform in all parts of the world, and at all heights above its surface, and nearly in all weathers (See DUMAS, *Essai de Statique Chimique*, 53; and M. B. LEWY on the Air of Copenhagen and Guadeloupe, &c., *Ann. Ch. et Ph.*, Août, 1843), and it has generally been considered as consisting of

	By measure.	By weight.
Oxygen	208	230
Nitrogen	792	770
	<hr/> 1000	<hr/> 1000

Though these are what are usually termed the *essential* component parts of atmospheric air, it contains other substances, which to a certain

extent may be regarded as adventitious, and the quantity of which is liable to vary*: of these, *carbonic acid and aqueous vapor* are the most important and constant. The quantity of the former may usually be considered as amounting to less than .01 per cent., namely from 3.7 to 6.2 measures in 10,000†. The presence of *aqueous vapor* in the atmosphere is shown in a variety of ways, but most easily by exposing to it certain deliquescent substances, which liquify or increase in weight in consequence of its absorption; and as the gases in general, unless artificially dried, also retain vapor of water, it is necessary, in delicate experiments, and in ascertaining their specific gravity, to take this ingredient into the account (see p. 367,) or to separate it by proper means. These processes are elsewhere detailed.

The relative quantity of aqueous vapor in the atmosphere is subject to much variation. From the experiments of Saussure, Dalton, and Ure, already referred to, it appears that 100 cubic inches of atmospheric air at 57°, are capable of retaining 0.35 grains of watery vapor; in this state the air may be considered at its maximum of humidity; it would also appear that all the gases take up the same quantity of water when under similar circumstances, and that it consequently depends, not upon the density or composition, but upon the bulk of the gas; and from Dalton's researches, it may be concluded that the vapor forms an independent atmosphere, mixed, but not combined with the air. (DANIELL'S *Meteorology*.)

Hygrosopes and *hygrometers* are instruments which show the presence of water in the air, its variation in quantity, and its actual quantity existing in a given bulk of air at any given time. Saussure employed a human hair, which, by its dilatations and contractions in moisture and dryness, turned an index; Deluc used a thin strip of whalebone in the same way; Wilson employed a rat's bladder, filled with mercury, and tied on to a large thermometer-tube: by its dilatation and contraction the mercury falls and rises in the tube, and thus indicates changes in the moisture of the air. Mason's hygrometer shows the relative dryness and moisture of the atmosphere by the degree of cold produced by evaporation from a given surface. If two delicate thermometers have their

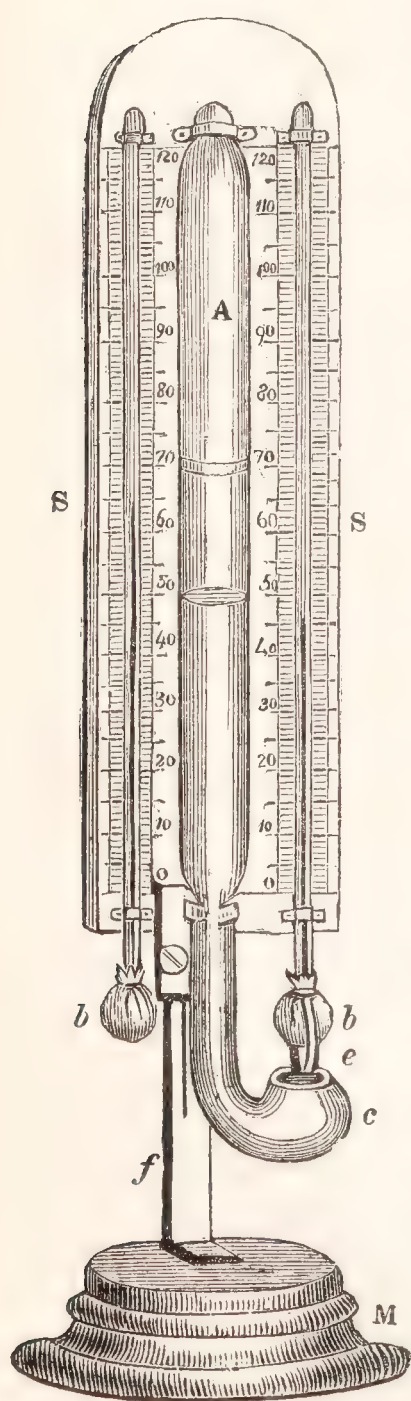
* Lavoisier's experiments gave 27 measures of oxygen and 73 nitrogen: Priestley stated the oxygen to vary from 20 to 25 *per cent.*: Cavendish estimated it at 20 *per cent.*: Berthollet found in the air of Cairo and of Paris 22 of oxygen: Saussure in Geneva 21 to 22: De Marty in Catalonia, in all situations, 21 to 22; Davy, at Bristol and upon the west coast of England, during westerly winds, 21. The same in air from the coast of Guinea. Berger on the Jura, and on the mountains and in the valleys of Savoy, 20.3 to 21.6: Configliachi on the Simplon 21, and in the Rice-fields of the Milanese 20.8: Gay Lussac, 22,000 feet above the surface, and in Paris, 21.49: Dalton in England 20.7 to 20.8: seldom 21; but on Jan. 8, 1825, Barom. 30.9 and wind north-east, 21.15.

Gay Lussac and Humboldt, instead of 21, as in the external air, found 20.2 in the Théâtre Français during the performance. (L. GMELIN, *Handbuch*, i. 443.)

† Saussure and Gay Lussac found the usual proportion of carbonic acid in the air from the summit of Mont Blanc, and 650 toises above Paris. Beauvais found scarcely a trace of carbonic acid in the air over the sea off Dieppe, but the usual proportion inland. According to Saussure, the proportion varies with the season: the air in a meadow, in August, contained 0.000713; in Jan., 0.000479; in Nov., in rainy and stormy weather, 0.000425. Dalton estimates the carbonic acid at 0.001; Configliachi the maximum at 0.008, and Humboldt (probably an excess) at 0.005 to 0.018. (L. GMELIN.)

bulbs covered with a thin piece of muslin, and if the one be dry and the other moist, the depression of the latter will be directly as the rapidity or amount of evaporation, and this again will chiefly depend upon the state of the circumambient air as to moisture: if it be charged with vapor, no evaporation from the wet bulb will ensue, and consequently the mercury in that thermometer will remain stationary: if, on the contrary, the air be very dry, it will eagerly abstract vapor from the humid surface, and a corresponding degree of cold will be indicated by the depression of the mercury in the humid thermometer, as compared with the standard or dry thermometer. The annexed wood-cut shows

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the arrangement of the thermometers in Dr. Mason's instrument. He covers the bulbs with white silk, and that intended for the hygrometric indications is kept constantly moist by the capillary action of a thread of floss silk which is attached to it, and of which one end dips into the cup of water forming the lower end of a reservoir, which acts upon the principle of the bird fountain. In this instrument the hygrometric degrees are best expressed by those of the thermometric scale.

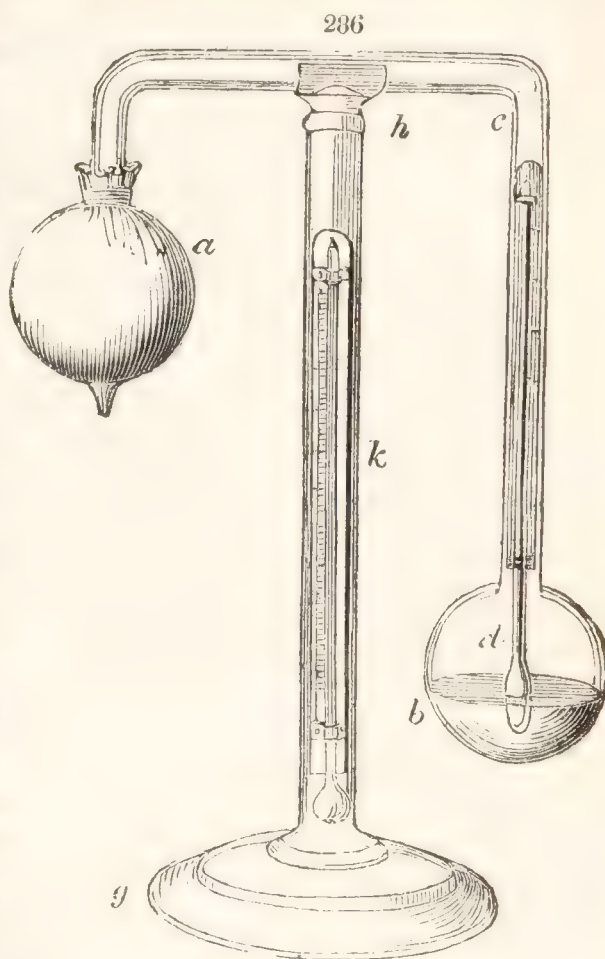
Daniell's hygrometer shows the constituent temperature of the moisture in the atmosphere, by its precipitation upon a cold surface; comparing this with the temperature of the atmosphere, the difference furnishes a datum for calculating the quantity of vapor in a given quantity of air. A detailed account of this instrument, and of the observations made with it, is given by Mr. Daniell in the *Quarterly Journal of Science* (vols. viii. ix. and x.), and in his "Essays." It consists of a tube, twice bent at right angles, at the ends of which are two thin glass bulbs; the one tightly covered by a piece of fine muslin, the other about half full of ether, and including a very delicate thermometer, the small oblong bulb of which is immersed into the ether, as shown in fig. 286. The bulbs and tubes are filled with the vapor of ether, to the entire exclusion of air, so that when the instrument is placed as in the figure, and the bulb *a* is cooled by dropping a few drops of good ether upon it, (see page 84 in reference to the phenomena of evaporation,

and the construction of the cryophorus, which acts upon the same principle,) the interior ethereal vapor is in part condensed, and the liquid in *b* furnishes a fresh portion, by which its temperature is more or less lowered, as shown by the immersed thermometer *d*. Now when the bulb *b* is thus cooled, it is in the condition of any other cold body, and has a tendency to cause the deposition of aërial moisture upon its surface; and the temperature at which such deposition will take place

or in other words the *dew-point*, will vary with the hygrometric state of the air. In very humid atmospheres the thermometer *d* will scarcely have fallen a degree before a ring of moisture is evident upon *b*, coinciding with the surface of the included ether, and being the point of lowest temperature: in dry atmospheres, on the other hand, it will be necessary to reduce the temperature of the included thermometer, by the continuous evaporation of ether from the covered bulb, many degrees, before the ring of dew is visible. Now the temperature at which this ring of dew is deposited, or the *dew-point*, may be accurately read off upon the interior thermometer by observing the degree at which it stands *at the moment of the first appearance of the ring of dew*; and this observation may be corrected or verified by again observing the temperature or degree at which *the ring of dew vanishes*: these two obser-

vations seldom differ more than a degree or two, and the mean may be assumed as correct, for the errors, if any, must lie in opposite directions. There is a second or external thermometer attached to this instrument at *k*, which shows the temperature of the air at the time of making the observation; and the difference between the two thermometers at that time gives the exact temperature required for the deposition of the aerial moisture, or is the dew-point; the extent of this difference is as the dryness of the air, and may thus be used as an hygrometric term. On one day, for instance, the external thermometer being 60° , the internal fell to 48° before the ring of dew appeared: on another day the external thermometer stood at 66° , and the internal had only fallen to 64° when the dew-ring appeared; here therefore the degree of dryness might be called 12° in the former, and 2° in the latter case. It is obvious then, in regard to this instrument, that it furnishes a very ready and exact method for the determination of the *dew-point*.

“By means of the dew-point accurately ascertained,” Mr. Daniell observes, “many points of the utmost interest to chemical and meteorological science may be determined. By mere inspection of tables properly constructed, we can at once determine the elasticity and density of the aqueous vapor—its weight in a cubic foot of the air—the degree of dryness, either upon the thermometric or the hygrometric scale—and the rate of evaporation; when the air is saturated, the precipitation is instantaneous, *i.e.*, the dew-point coincides with the temperature of the air. In this country, the degree of dryness measured in thermometric degrees seldom reaches 30° , that is to say, the dew-point is seldom 30° below the temperature of the air, but in the Deccan, with a temperature of 90° , the dew-point has been seen as low as 29° , making the degree of dryness 61° .



“The more accurate mode, however, of expressing the moisture of the air from an observation of the temperature and dew-point, is by the quotient of the division of the elasticity of vapor at the real atmospheric temperature, by the elasticity at the temperature of the dew-point: for, calling the term of saturation 1000, as the elasticity of vapor at the temperature of the air is to the elasticity of vapor at the temperature of the dew-point, so is the term of saturation to the observed degree of moisture. Thus, with regard to the observation in the Deccan,

Force at 60°

1·430

:

Force at 29°

0·194

::

1000

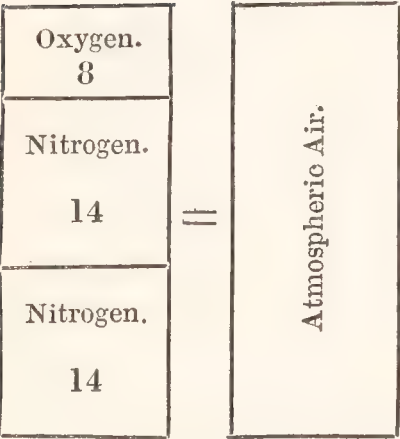
:

135.

“The fourth term is the degree of moisture on the hygrometric scale.”

As an average of results, the ordinary constituents of the atmosphere appear to be in the following proportions:

Nitrogen	78·8
Oxygen	19·7
Aqueous vapor	1·4
Carbonic acid	·1
	<hr/>
	100·0



If the relative bulk of oxygen to nitrogen be considered as 1 to 4, and many analysts will not allow that the atmosphere contains more than 20 of oxygen to 80 of nitrogen, it follows that, in reference to the atomic theory, it is a mixture of one atom or equivalent of oxygen=8, and two of nitrogen=14 × 2=28; as represented in the margin.

In addition to the substances above enumerated as the *constant* component parts of our atmosphere, it contains, in certain situations, minute quantities of what may be termed *accidental ingredients*, the nature and proportions of which depend upon a variety of causes; and “as the sea contains a little of everything that is soluble in water, so,” as Dr. Prout observes, “the atmosphere may be conceived to contain a little of everything that is capable of assuming the gaseous form.” It has even been supposed that all substances may impart in this way portions of foreign matter, which, though infinitely small, would in time accumulate into sensible proportions; the formation of *aërolites* has even been referred to such a cause: but the fallacy of this hypothesis has been satisfactorily demonstrated by Faraday (*On the existence of a Limit to Vaporisation*, *Phil. Trans.*, 1826, p. 484), his argument being founded on the principle by which Wollaston accounted for the limited extent of the atmosphere (*Phil. Trans.*, 1822, p. 89); namely, that its boundary is dependent upon the opposing powers of elasticity and gravitation. On passing upwards from the earth’s surface the air becomes more and more attenuated in consequence of the gradually diminishing pressure of the superincumbent part, and its tension or elasticity is proportionately diminished: when the diminution is such that the elasticity is a force not more powerful than the attraction of gravity, then a limit to the atmosphere

must occur: the particles of the atmosphere there tend to separate with a certain force, but this force is not greater than the attraction of gravity which tends to make them approach the earth and each other; and as expansion would necessarily give rise to diminished tension, the force of gravity would then be strongest, and consequently cause contraction, until the powers were balanced as before.

This condition of ærial particles, Faraday applies to all other vapors, and infers that every kind of matter ceases to assume the elastic form, when the gravitation of its particles exceeds the elasticity of its vapor; and by proving that a variety of substances, kept for some years in a confined space and with moisture, underwent no evaporation, he has furnished ample grounds for denying the existence of a miscellaneous collection of vapors in the atmosphere.

To revert, however, to the *extraneous matters*, as they may be called, which have actually been detected, or may fairly be presumed to exist in the air. One of these, to which much importance has been attached as the source of nitrogen in vegetables, is ammonia, probably as a carbonate: thus acids, exposed to the air, gradually imbibe traces of ammonia: solution of sulphate of alumina too, after long exposure, yields crystals of ammonia-alum. Pipe-clay heated to redness, and exposed for a week to the air, evolves ammonia when heated; but if preserved from the contact of air no trace of ammonia is offered. When rain or snow-water is distilled, the first portion which comes over contains carbonate of ammonia, and yields sal ammoniac on evaporation after the addition of a few drops of muriatic acid; the same salt is observable in almost all water after it has been similarly acidulated and evaporated. We observe, in London, that traces of sulphurous and sulphuric acid are observable, and also of sulphate of ammonia, which salt we sometimes see upon dirty windows in small stellated spots: these, as well as finely-divided carbonaceous matter, are no doubt derived from coal-smoke. So also, in regard to traces of sulphuretted hydrogen, indicated by the tarnish of silver: this contamination is subject to much variation, and often entirely local, as in the neighbourhood of gas-works, sewers, stagnant pools, sulphur springs, &c. The presence of a minute trace of free hydrogen has been suspected in the air, and also of that form of carburetted hydrogen known as fire damp, or marsh gas. The air in the vicinity of certain manufactories, reducing-furnaces, and other places where large quantities of peculiar gases or vapors may be generated, will also be liable to more or less *local contamination*. In the vicinity of the sea, and especially during storms, the rain which falls contains traces of salt, and during a thunder-storm it may possibly afford slight indications of nitric acid and nitrate of ammonia (p. 336). Sometimes rain and snow have been colored by extraneous matters, mechanically diffused through the air; this has occasionally been traced to minute lichens, and other cryptogamous plants, brought from a distance by the winds, and diffused in myriads through the atmosphere; and sometimes to volcanic dust composed of earthy and metallic matters in a state of extreme comminution. The substances foreign to our atmosphere, and held in it in what may be termed a state of solution, are probably more numerous and various, though little understood, and from their nature, and the minute quantities

in which they exist, very difficult of detection or examination. Various forms of *infection*, and *malaria* or *marsh-miasma*, are instances of such contaminations, and it is not improbable, from the manner in which they appear to be decomposed and destroyed by chlorine, that they consist of some organic or hydrogenated compounds. When solution of nitrate of silver is exposed to air, or when it is mixed with rain water and subjected to light, it becomes reddish, and deposits a precipitate in consequence of the presence of organic matter: but this is probably derived from the minute particles of dust floating in the air, and not from any *peculiar* organic matter, as the *pyrrhin* of Zimmerman: odorous matter, such as the odor of flowers, perfumes, &c., may contribute to this influence. Dr. Prout (*Bridgewater Treatise*, p. 350,) has suggested the possibility of some form of selenium being occasionally present in the air, so as to produce catarrhal epidemics, and in favor of the production of diseases by some such foreign matters, adduces the following observations which occurred to him during the presence of the epidemic cholera. "He had for some years been occupied in investigations regarding the atmosphere, and for more than six weeks previous to the appearance of cholera in London, had almost every day been engaged in endeavoring to determine with the utmost possible accuracy the weight of a given quantity of air, under precisely the same circumstances of temperature and pressure. On a particular day, the 9th of February, 1832, the weight of the air suddenly appeared to rise above the usual standard. As the rise was at the time supposed to be the result of some accidental error, the succeeding observations were made with the most rigid scrutiny. On the days immediately following, the weight of the air still continued above the standard, and retained its augmented weight during the whole time the experiments were carried on, namely, about six weeks longer: the increase of weight was small, but still decided and real." Dr. Prout then goes on to state, that on the 9th of February the wind, which had been previously west, veered round to the east, and that precisely on the change of the wind, the first cases of the epidemic cholera were reported in London, and that from that time the disease continued to spread. I bring forward these observations not only as curious in themselves, but as showing, at least one cause of a possible discrepancy in the different estimates of the specific gravity of atmospheric air.

The extraordinary fact of the uniform constitution of the atmosphere in reference to the relative proportion of its oxygen, notwithstanding the constant conversion of the latter into carbonic acid by the processes of respiration and combustion, is apparently accounted for by the restitution of oxygen derived from the decomposition of carbonic acid effected by the functions of plants, the green parts of which, under the influence of light, are constantly performing this salutary office. It appears, however, from the observations of Saussure, that such is the enormous bulk of the atmosphere, that even if there were no restorative or renovating agencies of this kind going on, it would be extremely difficult to discover any sensible differences in its composition resulting from the above causes, which

* For the analysis of air from a variety of confined situations, see F. LEBLANC, *Ann. Ch. et Ph.*, v. 223, 3me Serie.

might be operative for many centuries without injurious effects, or at least without occasioning such change in the whole mass as to be detected by delicate analysis. In these speculations it must also be remembered that the different parts of the atmosphere are constantly kept in a uniform state of mixture, by the propensity which gaseous bodies have, notwithstanding material differences in their specific gravities, to diffuse themselves equably through each other, and that this equality of mixture is further promoted by the constant agitation to which the air is subjected by winds, and by the varied temperature of different portions of the earth's surface.

The combustion of substances in the air under ordinary circumstances will be explained by reference to the details given in the chapters on Heat and on Oxygen. Some peculiar cases of combustion, however, which require more extended notice, have been ingeniously investigated by H. Davy. (*Essay on Flame*, and *Phil. Trans.*, 1817.) In examining, for instance, the effect of *rarefaction* upon combustion, he found that when hydrogen gas was inflamed at a fine orifice, so as to make a jet of flame of about one-sixth of an inch in height, and introduced under the receiver of an air-pump containing from 200 to 300 cubical inches of air, the flame enlarged as the receiver became exhausted; and when the gauge indicated a pressure between four and five times less than that of the atmosphere, was at its maximum of size; it then gradually diminished below, but burned above, till the pressure was between seven and eight times less, when it became extinguished.

To ascertain whether the effect depended upon the deficiency of oxygen, he used a larger jet with the same apparatus, when the flame burned longer, and this when the atmosphere was rarefied ten times. When the larger jet was used, the point of the glass-tube became white-hot, and continued red-hot till the flame was extinguished. It therefore occurred to him, that the heat communicated to the gas by this tube, was the cause that the combustion continued longer in the last trials when the larger flame was used; and the following experiments confirmed the conclusion. A piece of wire of platinum was coiled round the top of the tube, so as to reach into and above the flame. The jet of gas of one-sixth of an inch in height was lighted, and the exhaustion made; the wire of platinum soon became white-hot in the centre of the flame, and a small point of wire near the top fused; it continued white-hot till the pressure was six times less; when it was ten times less it continued red-hot at the upper part, and as long as it was dull red, the gas, though extinguished below, continued to burn in contact with the hot wire, and the combustion did not cease till the pressure was reduced thirteen times.

It appears from this result, that the flame of hydrogen is extinguished in rarefied atmospheres, only when the heat it produces is insufficient to keep up the combustion, which appears to be when it is incapable of communicating visible ignition to metal, and as this is the temperature required for the inflammation of hydrogen at common pressures, it appears that its *combustibility* is neither diminished nor increased by rarefaction from the removal of pressure.

According to this view with respect to hydrogen, it should follow that, amongst other combustible bodies, those which require least heat

for their combustion ought to burn in more rarefied air than those that require more heat; and those that produce much heat in their combustion ought to burn, other circumstances being the same, in more rarefied air than those that produce little heat; and Sir Humphry's experiments confirm these conclusions. Thus, olefiant gas, which approaches nearly to hydrogen in the heat produced by its combustion, and which does not require a much higher temperature for its inflammation, when its flame was made by a jet of gas from a bladder connected with a small tube furnished with a wire of platinum, under the same circumstances as hydrogen, ceased to burn when the pressure was diminished between ten and eleven times; and the flames of alcohol and of a wax-taper, which require a greater consumption of heat for the volatilization and decomposition of their combustible matter, were extinguished when the pressure was five or six times less without the wire of platinum, and seven or eight times less when the wire was kept in the flame. Light carburetted hydrogen (fire-damp) which produces less heat in combustion than any of the common combustible gases, except carbonic oxide, and which requires a higher temperature for its inflammation than any other, had its flame extinguished, even though the tube was furnished with a wire, when the pressure was below one-fourth.

The flame of carbonic oxide, which, though it produces little heat in combustion, is as inflammable as hydrogen, burned when the wire was used, the pressure being one-sixth.

The flame of sulphuretted hydrogen, the heat of which is in some measure carried off by the sulphur produced by its decomposition during its combustion in rare air, when burned in the same apparatus as the olefiant and other gases, was extinguished when the pressure was one-seventh.

Sulphur, which requires a lower temperature for its combustion than any common inflammable substance, except phosphorus, burned with a very feeble blue flame in air rarefied fifteen times, and at this pressure the flame heated a wire of platinum to dull redness, nor was it extinguished till the pressure was reduced to one-twentieth*.

Phosphorus, as has been shown by Van Marum, burns in an atmosphere rarefied sixty times; and Sir Humphry found that phosphuretted hydrogen produced a flash of light when admitted into the best vacuum that could be made by an excellent pump of Nairn's construction.

The mixture of chlorine and hydrogen inflames at a much lower temperature than that of hydrogen and oxygen, and produces a considerable degree of heat in combustion; it was therefore probable that it would bear a greater degree of rarefaction, without having its power of exploding destroyed; and this was found by many trials to be the case, contrary to the assertion of Grotthus. Oxygen and hydrogen, in the proportion to form water, will not explode by the electrical spark when rarefied eighteen times; but hydrogen and chlorine in the proportion to

* The temperature of the atmosphere diminishes in a certain ratio with its height, which must be attended to in the conclusions respecting combustion in the upper regions of the atmosphere, and the elevation must be somewhat lower than in arithmetical

progression, the pressure decreasing in geometrical progression. There is, however, every reason to believe that the taper would be extinguished at a height of between 9 and 10 miles, hydrogen between 12 and 13, and sulphur between 15 and 16.

form hydrochloric acid gas, gave a distinct flash of light under the same circumstances, and they combined with visible inflammation when the spark was passed through them, the exhaustion being to one-twenty-fourth.

The experiment on the flame of hydrogen with the wire of platinum, and which holds good with the flames of other gases, shows, that by preserving heat in rarefied air, or giving heat to a mixture, inflammation may be continued, when, under common circumstances, it would be extinguished. This was found to be the case in other instances, when the heat was differently communicated: thus, when camphor was burned in a glass tube, so as to make the upper part of the tube red-hot, the inflammation continued when the rarefaction was nine times, whereas it would only continue in air rarefied six times, when it was burned in a thick metallic tube which could not be considerably heated by it. (DAVY *on Flame*, p. 56.)

The influence of the admixture of other gases with atmospheric air upon its power of supporting combustion, is another subject which has been elucidated by Davy's experiments. He found that a wax-taper was instantly extinguished in air mixed with one-tenth of silicated fluoric acid gas, and in air mixed with one-sixth of hydrochloric acid gas; but the flame of hydrogen burned readily in those mixtures; and in mixtures in which the flame of hydrogen was extinguished the flame of sulphur burned.

The following simple experiment demonstrates this general principle. Into a long bottle with a narrow neck introduce a lighted taper, and let it burn till it is extinguished; carefully stop the bottle, and introduce another lighted taper; it will be extinguished before it reaches the bottom of the neck; then introduce a small tube containing zinc and diluted sulphuric acid, at the aperture of which the hydrogen is inflamed; the hydrogen will be found to burn in whatever part of the bottle the tube is placed; after the hydrogen is extinguished, introduce lighted sulphur; this will burn for some time; and after its extinction, phosphorus will be as luminous as in the air, and, if heated in the bottle, will produce a pale-yellow flame of considerable density.

In cases when the heat required for chemical union is very small, as in the instances of hydrogen and chlorine, a mixture which prevents inflammation will not prevent combination, *i. e.*, the gases will combine without any flash. Thus, in mixing two volumes of carburetted hydrogen with one of chlorine and hydrogen, hydrochloric acid was formed throughout the mixture, and heat produced, as was evident from the expansion when the spark passed, and the rapid contraction afterwards, but the heat was so quickly carried off by the quantity of carburetted hydrogen that no flash was visible.

Steam, and such vapors as require considerable heat for their formation, have a less power of preventing combustion than permanent gases. Sir H. Davy found that a very large quantity of steam was necessary to prevent sulphur from burning. Oxygen and hydrogen exploded by the electric spark, when mixed with five times their volume of steam; and even a mixture of air and carburetted hydrogen gas, the least explosive of all mixtures, required a third of steam to prevent its explosion; whereas one-fifth of nitrogen produced the effect. (DAVY *on Flame*, p. 87.)

In the course of the above experiments, Sir Humphry endeavoured to ascertain what would be the effect of *condensation* on flame in atmospheric air, and whether the cooling power of the nitrogen would increase in a lower ratio, as might be expected, than the heat produced by the increase of the quantity of matter entering into combustion. He found considerable difficulties in making the experiments with precision; but he ascertained that both the light and heat of the flames of the taper, of sulphur and of hydrogen, were increased in air condensed four times, but not more than they would have been by an addition of one-fifth of oxygen.

He condensed air nearly five times, and ignited iron-wire to whiteness in it by the Voltaic apparatus, but the combustion took place with very little more brightness than in the common atmosphere, and would not continue as in oxygen; nor did charcoal burn much more brightly in this compressed air than in common air. These experiments show that (for certain limits at least), as rarefaction does not diminish considerably the heat of flame in atmospheric air, so neither does condensation considerably increase it; a circumstance of great importance in the constitution of our atmosphere, which at all the heights or depths at which man can exist still preserves the same relation to combustion.

§ VIII. SULPHUR. S. 16.

SULPHUR, or *brimstone*, is a brittle substance, of a pale-yellow color, somewhat translucent, insipid, and inodorous, but exhaling a peculiar odor when heated. The ancients used it in medicine, and its fumes were employed in bleaching wool. (PLINY, lib. xxxv. cap. 57.) Its specific gravity is 1·970, to 2·080. Its specific heat, as determined by Dulong and Petit, 0·1880. According to Regnault, the specific heat of crystallized native sulphur is 0·1776, and of sulphur recently fused, 0·1844. It becomes negatively electrical by heat and by friction, and is a non-conductor of electricity*.

Sulphur is chiefly a mineral product, and occurs crystallized, its primitive form being an acute octohedron with a rhombic base. In this state its sp. gr. is 2·045, and the crystals are in a high degree doubly refractive. According to Mitscherlich, it has, when artificially crystallized, as when suffered gradually to cool after having been fused, a different primitive form, namely, an oblique rhombic prism. From its solutions in alcohol, ether, sulphuretted carbon, and chloride of sulphur, it is generally deposited in the octohedral form. Crystals of native sulphur which have been formed by the condensation of sulphur vapor, as well as those which are deposited from a solution of sulphur in any men-

* Sulphur, in its ordinary state, always contains traces of hydrogen, which it gives off during the action of various bodies for which it has a powerful attraction. Thus, if equal weights of sulphur and copper, or iron-filings, be introduced into a retort, and heated, a portion of sulphuretted hydrogen is evolved at the period of their combination. When potassium and sulphur

are heated together, a vivid combustion ensues, and a little sulphuretted hydrogen is evolved. Berzelius, by heating sulphur with oxide of lead, remarked the formation of water, but in such small and indefinite quantities, as induced him to adopt the generally received opinion, that the presence of hydrogen is accidental, and that it is not an element of sulphur.

struum, possess forms which are either identical, or connected by being referable to the same crystalline axes. Such, on the contrary, as are produced by the cooling of fused sulphur, belong to a different system of crystallization. The condition determining the form is temperature: if the crystal be formed below 232° it belongs to the right prismatic system; if at that point, to the oblique prismatic. This is proved by the influence of temperature on a crystal of either system; a crystal of fusion, when first formed, is perfectly clear and transparent, but kept at common temperatures it soon becomes opaque, and presents the appearance of the roll-sulphur of commerce: the same change occurs when a native crystal is placed in a solution of salt which boils at 232° . The opacity is in both cases produced by a new arrangement of the particles of sulphur, by which, without any change in the exterior form, the internal structure of the crystal is altered to correspond to the crystallization peculiar to the temperature. Sulphur, therefore, is dimorphous.

Native sulphur is principally brought to this country from Sicily, where it occurs in beds, in a blue clay formation, occupying the central half of the south coast of the island, and extending inwards as far as the district of Etna. This blue clay formation is considered by Dr. Daubeny of the same age with the gypsum bed of Paris, and therefore more recent than chalk. It contains beds of gypsum and of salt, and the sulphur is in some places associated with splendid crystals of sulphate of strontia. The supply of sulphur derived almost exclusively from Sicily is enormous: the average annual importation into England is between 16 and 17 thousand tons, at from 6*l.* to 10*l.* per ton. It undergoes a rough purification by fusion, and is brought into the market in square or oblong masses or blocks. At Bex, in Switzerland, sulphur occurs in the gypsum of the salt deposit; and it is found in the same rock in many other parts of Europe, generally in beds or masses; in Suabia, and near Schemnitz in Hungary, it is found in veins traversing granite and mica slate; and in the same rocks in Quito in Peru: near Gibraltar, it occurs in fetid limestone. Sulphur is also common in the fissures of lava near volcanic craters: there is a great deposit of this species of sulphur in the plain of the Solfatara near Naples. Sulphur is found abundantly combined with certain metals; the common ores of lead and copper are their *sulphurets*; sulphuret of iron, or *pyrites*, is also a very common mineral.

Sulphur is insoluble in water, and suffers no change by exposure to air. When heated to about 180° , it volatilizes, and its peculiar odor is strong and disagreeable; at about 220° it begins to fuse, and between 230° and 270° , it is perfectly liquid, and of a bright brownish-yellow color; between 300° and 500° it becomes viscid, and of a brown color, but regains its fluidity when cooled; at higher temperatures (out of the contact of air) it again becomes more liquid, and at about 600° it boils, and sublimates in the form of an orange-colored vapor, and may be condensed either in a solid or pulverulent state, according to the rapidity of the process and the size of the condensing vessels. The residue is the *sulphur vivum* of old pharmacy. When sulphur, which has been heated to about 300° , is poured into warm water, it acquires the consistency of soft wax, and hardens on cooling. In this state it is sometimes used to take impressions of gems and medals; it is of a reddish color, and of the specific gravity 2.3. When slowly cooled after fusion, sulphur forms a

fibrous crystalline mass; but it sometimes retains its fluidity, and does not concrete till touched by some solid body. This state appears somewhat analogous to that of water cooled in a quiescent state below its freezing-point. (FARADAY. *Quarterly Journal*, xxi. 392.) The following table shows the results of Dumas's experiments on the influence of temperature upon the color and properties of sulphur:—

Temperature.			Hot Sulphur.	Sulphur suddenly cooled by immersion in water.
Fahr.	Cent.			
230°	110°	Very liquid : yellow	Very friable : usual color
284	140	Liquid : deep yellow	Do. do.
338	170	Thick : orange yellow	Friable : do.
374	190	Thicker : orange	{ At first soft and transparent, then friable and opaque : usual colour
428	220	Viscid : reddish	Soft : transparent : amber color
464 to 500	240 to 260		Very viscid : brown-red	Very soft : transparent : reddish
	Boiling-pt.		Less viscid : brown-red	Do. do. brown-red.

In order that sulphur may retain its soft or viscid state it is not necessary, as sometimes directed, to keep it long in a fused state, but merely to take care that it has been raised to a due temperature and then suddenly cooled by dropping it into cold water; if poured into the water in mass, the interior cools slowly and reverts to its brittle state: here, therefore, the effect of what may be called *tempering* is the reverse of that produced upon steel, and somewhat corresponds with the phenomena presented by bronze.

Sulphur is commonly met with in three forms; namely, 1. *Massive* or native sulphur, already mentioned. 2. *Stick* or *roll* sulphur, which is chiefly obtained from sulphuret of copper in this country, and elsewhere abundantly from sulphuret of iron, or common pyrites; these ores are roasted, and the fumes received into a long chamber of brickwork, where the sulphur is gradually deposited; it is then purified by fusion, and cast into sticks. In this state, if grasped by the warm hand, it splits with a crackling noise. 3. *Sublimed* sulphur, or *flowers of sulphur*, which is in a pulverulent form, and procured by condensing the vapor of sulphur rapidly in capacious receivers; it is of a peculiar pale yellow color, and when examined by a microscope appears composed of minute opaque flattened spheres not having a crystalline fracture (FRITZSCHE); it is always somewhat sour, and therefore for certain pharmaceutical purposes is directed to be washed with hot water.

The sulphur of commerce occurs in three prevailing colors, namely, lemon yellow verging on green, dark yellow, and brown yellow; these shades result, partly at least, as the above table shows, from the different degrees of heat to which it has been exposed during its fusion or extraction on the great scale, the palest variety having been the least heated. The different modes of purifying sulphur are described by Dr. Ure in the first volume of the *Royal Inst. Journal*. (For a detailed account of the methods of obtaining and purifying sulphur, see also DUMAS: *Chimie appliquée aux Arts*.)

For some pharmaceutical purposes sulphur is precipitated from its alkaline solutions by an acid, and, when washed and dried, is in the form of a yellowish-grey impalpable powder; this is the *milk of sulphur* and *precipitated sulphur* of the *Pharmacopœia*. Thomson considers it

as a compound of sulphur and water. (*System of Chemistry*, vol. i. p. 285;) but when dried, it gives out no water, but fuses into common sulphur, always, however, evolving a little hydrogen.

The purity of sulphur may be judged of by heating it gradually upon a piece of platinum leaf; if free from earthy impurities, it should totally evaporate. It should also be perfectly soluble in boiling oil of turpentine. According to Ure, sulphur is soluble in ten times its weight of boiling oil of turpentine at 316° , forming a solution which remains clear at 180° . As it cools to the atmospheric temperature, crystalline needles form, which may be washed with cold alcohol or tepid water. The usual impurities of sulphur are carbonate and sulphate of zinc, oxide and sulphuret of iron, sulphuret of arsenic, and silica, and remain unaffected by the volatile oil.

Sulphur dissolves with some difficulty, and in very small proportions, in alcohol; to effect this solution both substances should be brought together in the state of vapor. It is more soluble in sulphuric ether.

It appears from the statements of Dumas and of Mitscherlich that the density of sulphur vapor is 6.65 (*Ann. Ch. et Ph.*, L. 170, and LV. 5), so that supposing it to exist in the state of vapor at mean temperature and pressure, 100 cubic inches would weigh 206.32 grains, and its specific gravity to hydrogen would be as 96 to 1.

When heated in the atmosphere to about 500° (DALTON) 560° (THOMSON,) sulphur inflames and burns with a peculiar blue light; at a higher temperature its vapor kindles with a purple flame; and in oxygen it burns vividly, with a large lilac-colored flame. The comparatively low temperature at which sulphur first kindles is an important circumstance in many of its applications, as for matches, gunpowder, &c. It may be well illustrated by propelling powdered sulphur into the hot air issuing from an argand lamp-glass; it takes fire at a great height above the flame.

SULPHUR AND OXYGEN. Four definite compounds of sulphur and oxygen, all of which rank among the acids, have long been known: namely, 1. Sulphurous acid; 2. Sulphuric acid; 3. Hyposulphurous acid; 4. Hyposulphuric acid. The existence of a fifth acid of sulphur has been indicated by Langlois (*Ann. Ch. et Ph.*, 3 Ser. iv. 77,) which he proposes to call *sulphyposulphuric acid*; and Fordos and Gélis have announced a sixth, which they term *bisulphuretted hyposulphuric acid*. There are, therefore, six oxyacids of sulphur, namely:

Sulphurous acid	SO ₂	Hyposulphuric acid	S ₂ O ₅
Sulphuric acid	SO ₃	Sulphuretted hyposulphuric acid	S ₃ O ₅
Hyposulphurous acid	S ₂ O ₂	Bisulphuretted hyposulphuric acid	S ₄ O ₅

Berzelius arranges these acids under four heads, as including respectively, 1, 2, 3, and 4 atoms of sulphur; he terms them *monothionic*, *dithionic*, *trithionic*, and *tetrathionic* acids.

SULPHUROUS ACID. SO₂. This acid was first examined by Stahl, who called it *phlogisticated sulphuric acid*. Scheele, in 1774, pointed out a method of obtaining it; and about the same time, Priestley procured it in the gaseous form, and ascertained its leading properties. Berthollet examined it in 1782, and 1789 (*Mem. Paris*, 1782, and *Ann.*

de Chim., ii. 54); and in 1797 Fourcroy and Vauquelin published a detailed series of experiments upon it. (*Ann. de Ch.*, xxiv. 229.) Some experiments on it were also published by Dr. Thomson in 1803. (NICHOLSON'S *Journal*, vi. 93.) Its atomic composition was first accurately investigated by Davy, by Gay Lussac, and by Berzelius.

At common temperatures and pressures sulphurous acid is a gaseous body, which may be obtained by several processes. It may be procured directly, by burning sulphur in oxygen gas; or indirectly, by boiling two parts of copper filings or of mercury in three of sulphuric acid; ($\text{Cu} + 2 [\text{SO}_3, \text{HO}] = \text{CuO}, \text{SO}_3, 2 \text{HO} + \text{SO}_2$); or by heating in a retort, a mixture of five parts of black oxide of manganese and one of sulphur. It must be collected and preserved over mercury; for water takes up rather more than thirty times its bulk of this gas. For all the common purposes of experiment it may be collected by displacement in dry stopper-bottles, as directed at page 269. It is often generated by the action of charcoal, wood, and various organic matters upon sulphuric acid, but in those cases it is mixed with carbonic acid.

The specific gravity of sulphurous acid gas is 2.2186, (2.2105, TURNER; 2.222, THOMSON;) and 100 cubical inches weigh 68.776 grains. (At 60° and 30 inches Bar., 68.691 grains. TURNER.) At 32°, 72.8660 grains. (THOMSON.) Its specific gravity compared with hydrogen is as 32 to 1.

Sulphurous acid is one of the most easily condensible of the gases. Monge and Clouet found, that at the freezing-point, and under pressure, it assumed a liquid form; the experiments of Faraday place the pressure required for this purpose at two atmospheres. Bussy (*Ann. of Phil.*, viii. 307, N.S.) has shown that this acid may be obtained in the liquid form at common atmospheric pressure, by passing it through tubes surrounded by a freezing mixture of salt and snow. (FARADAY'S *Manipulation*, p. 215.) In this state it is a limpid liquid of the sp. gr. of 1.45. It boils at 14°, and evaporates with such rapidity at common temperatures as to generate a great degree of cold, so that by its aid mercury may be frozen, and chlorine, ammonia, and cyanogen liquified. It conducts electricity (KEMP) (not when perfectly dry, DELARIVE.) When exposed, in a humid state, to cold, a crystalline solid is formed, containing about 20 per cent. of water (perhaps 1 equivalent of acid + 1 of water.) A similar compound is often observed to invest the bubbles of gas produced by pouring the liquid acid into water.

When liquid sulphurous acid is allowed to evaporate in vacuo, the cold produced is so intense that it congeals; it may also be frozen by the aid of a mixture of solid carbonic acid and ether: it then forms a white mass, denser than the liquid acid. A table of the tension of its vapor from 0° to 110° is given by Faraday. (*Phil. Trans.*, 1815, 164.)

When sulphur is burned in pure and perfectly dry oxygen, sulphurous acid is produced, without any change in the volume of the gas, so that its composition is learned by the increase of weight; and as 100 cubic inches of oxygen dissolve between 34 and 35 grains of sulphur, it is obvious that sulphurous acid is composed of equal weights of sulphur and oxygen. According to Mitscherlich's estimate of the specific gravity of sulphur vapor, sulphurous acid consists of 100 volumes of oxygen gas, and 16 of the vapor of sulphur, condensed into 100 volumes: or one volume

of oxygen combined with one-sixth of a volume of sulphur vapor constitute one volume of sulphurous acid.

						Berzelius.
Sulphur	1	...	16	...	50	49·968
Oxygen.....	2	...	16	...	50	50·032
<hr/>						<hr/>
Sulphurous acid	1	...	32	...	100	100·000

	Volume.	Sp. Gr.	S		
Sulphur vapor.....	$\frac{1}{6}$	16	0	SO ₂ 32
Oxygen gas.....	1		8	
<hr/>				0	
Sulphurous acid gas	1		8	

Sulphurous acid gas has a suffocating odor; it is fatal to animal life, and extinguishes most combustibles when immersed into it in an inflamed state: hence it is sometimes resorted to for extinguishing burning soot in a chimney, as by throwing a handful of sulphur into the fire: it vividly maintains the combustion of potassium and sodium. At mean temperature and pressure, recently-boiled water takes up about 33 volumes (37, GRAHAM) of sulphurous acid gas. This solution, (*aqueous sulphurous acid*), is often required in the laboratory, and may be economically procured by filling a Florence flask about three-fourths with coarsely-bruised charcoal drenched in sulphuric acid, and applying the heat of a lamp; the gases evolved, which are sulphurous and carbonic acid, may be conducted by a bent tube into a bottle of water, when the carbonic acid escapes, but the water becomes a saturated solution of sulphurous acid: it has a sulphurous and somewhat astringent taste, and it bleaches many vegetable colors; but, by keeping, it acquires a sour flavor, and reddens the generality of vegetable blues. Upon some coloring matters, as that of cochineal, it has little action; and when it does destroy color, the original tint may often be restored by a stronger acid. A red rose, for instance, or the infusion of red rose leaves, is bleached by solution of sulphurous acid; but the color is restored by dilute sulphuric acid. According to Grotthus, the sulphurous acid and certain coloring matters combine into colorless compounds, which are decomposed by more powerful acids. A singular bleaching effect is produced upon some flowers by burning a little sulphur, so that the fumes of the sulphurous acid may come into contact with their petals: the dark-colored dahlias, and heart's-ease, may thus be amusingly variegated. Obtained by burning sulphur, this acid is much used in bleaching cotton goods (*Quarterly Journ. of Science*, iv. 196), also for whitening silk and wool, and altering the color of hops.

When the aqueous solution of sulphurous acid is boiled, a great part of the gas escapes, but not when it is frozen. Its specific gravity at 60°, when it contains 33 volumes of the gas, is 1·05 (THOMSON). Alcohol dissolves sulphurous acid more copiously than water; one volume taking up more than 100 of the gas.

Anhydrous sulphurous acid, in its liquified state (that is, the *condensed gas*), is not an electrolyte, but when dissolved in water the solution yields oxygen at the anode, and hydrogen and sulphur at the cathode. A solution containing sulphuric acid in addition, is a better conductor: it gives very little gas at either electrode: that at the anode is oxygen, that at the

cathode pure hydrogen, and from the cathode arises a white turbid stream consisting of diffused sulphur. "I conclude that the sulphurous acid was not affected by the electric current, and that the water only was electrically decomposed: that at the anode the oxygen from the water converted the sulphurous into sulphuric acid; and at the cathode, the hydrogen, electrically evolved, decomposed the sulphurous acid, combining with its oxygen, and setting the sulphur free: that the sulphur at the negative electrode was only a secondary result." (FARADAY, *Phil. Trans.*, 1834, p. 97.)

Sulphurous acid gas suffers no change at a red-heat; but if mixed with hydrogen, and passed through a red-hot tube, water is formed and sulphur deposited; under the same circumstances, it is also decomposed by charcoal, by potassium, and sodium, and probably by several other metals. It undergoes no change when mixed with oxygen, unless humidity or water be present, in which case a portion of sulphuric acid is slowly formed. When mixed with chlorine, and in contact with water, sulphurous acid gives rise to sulphuric and hydrochloric acid, but the perfectly dry gases have no mutual action, except under the influence of bright summer sunshine, when a mixture of equal volumes of chlorine and sulphurous acid yield a fluid of the specific gravity 1.659 at 68°, which boils at 170°, the specific gravity of the vapor being 4.67. Its formula is SO_2Cl . It may be compared to sulphuric acid, of which 1 atom of oxygen is replaced by 1 of chlorine. With water it evolves heat and yields hydrochloric and sulphuric acids: $\text{SO}_2\text{Cl} + \text{HO} = \text{SO}_3 + \text{HCl}$. (REGNAULT, *Ann. Ch. et Ph.*, LXIX. and LXXI.) Iodine and bromine are without action on sulphurous acid unless water be present, when sulphuric acid, and hydriodic and hydrobromic acids are formed. The chloric, bromic, and iodic acids are decomposed by sulphurous acid, with the evolution of chlorine, bromine, and iodine, and the formation of sulphuric acid. When gaseous sulphurous acid is mixed with hydrochloric, hydriodic, or hydrobromic acid gases, they mutually decompose each other; water, and chloride, iodide and bromide of sulphur, are formed; but when these acids are in aqueous solution they then do not decompose each other. In the presence of certain bases, sulphurous acid and nitric oxide combine to form crystalline compounds. Peroxide of lead, or of manganese, added to the aqueous solution of sulphurous acid, convert it into sulphuric acid, and destroy its odor. (On the use of sulphurous acid and sulphites in analysis, see WACKENRODER, *Chem. Gaz.*, Jan. 1843; BERTHIER, *ibid.*, April, 1843; and *Ann. Ch. et Ph.*, Jan. 1843.)

Vapor baths, in which sulphurous acid with or without steam is applied to the surface of the body, have been resorted to in the treatment of certain cutaneous complaints, and in rheumatic and other painful affections. The arrangements for this purpose employed in Paris are described and depicted by Dumas, (*Chimie app. aux Arts*; see also PEREIRA, *Elements of Materia Medica*.)

The greater number of the *sulphites* when exposed in a moist state to the air, pass, by absorption of oxygen, into sulphates; chlorine, nitric acid, and several other oxidizing agents, produce the same change: they discolor the solution of manganate of potassa, and reduce the persalts of iron to the state of protosalts; added to nitrate of silver they form at first a

white precipitate of sulphite of silver, which when boiled is partly resolved into metallic silver: they also reduce the acid solution of chloride of gold.

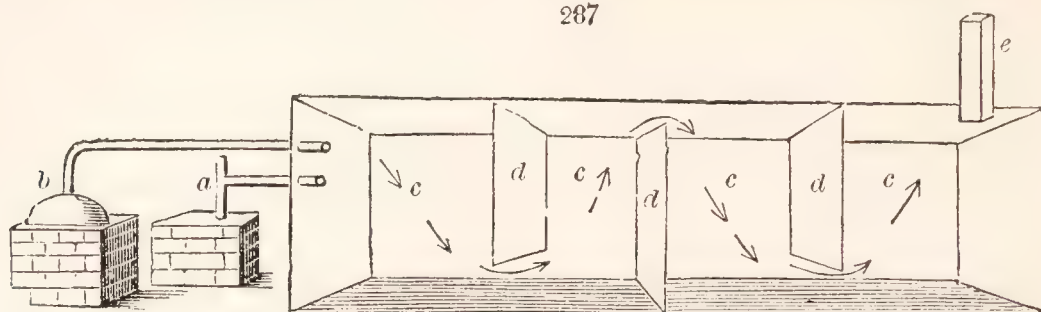
SULPHUROUS ACID AND AMMONIA. SULPHITE OF AMMONIA. $\text{NH}_3, \text{SO}_2, \text{HO}$. When sulphurous acid gas is passed into aqueous solution of ammonia, a sulphite of ammonia is formed, which may be obtained in six-sided prismatic crystals of a pungent sulphurous taste; exposed to air they absorb oxygen, and pass into sulphate of ammonia: heated out of contact of air they yield water, ammonia, and a sublimate of acid sulphite. Sulphite of ammonia is very soluble in water, and produces cold during its solution.

SULFIMIDE. The mutual action of dry sulphurous acid and ammonia has been studied by Rose: when these gases, deprived of humidity, are combined, they produce deep yellow crystals, which contain the elements of 1 atom of ammonia and 1 atom of sulphurous acid: when there is great excess of sulphurous acid gas present, a compound in which equal volumes are condensed, and which therefore corresponds to a bisulphite of ammonia, is obtained; but no basic compound can be obtained by the employment of any excess of ammonia. The neutral compound has been chiefly examined by Rose; it is termed by Dumas, *Sulfimide*. (*Chim. app. aux Arts*, v. 709.) Exposed to the air, it becomes white, deliquesces, and gradually passes into sulphate and hyposulphite of ammonia; and although to some tests it presents the characters of a sulphite of ammonia, with others, and especially with nitrate of silver, it acts as a hyposulphite. Dumas considers it as a hydrated amide, having the formula $\text{NH}_2, \text{SO}, \text{HO}$: these elements are equivalent to those of an anhydrous sulphite of ammonia, and would indicate the condensation of 2 volumes of ammonia and 1 of sulphurous acid gas $= \text{NH}_3, \text{SO}_2$.

SULPHURIC ACID. SO_3 . OIL OF VITRIOL. PROTOHYDRATE OF SULPHURIC ACID. SULPHATE OF WATER. HO, SO_3 , or H, SO_4 . This important acid was formerly obtained by the distillation of sulphate of iron, or *green vitriol*, and was, therefore, termed *oil of vitriol*. It is now almost exclusively procured in this country by the combustion of a mixture of about eight parts of sulphur and one of nitre. (The quantity of nitre or of nitrate of soda used, varies from one eighth to one twentieth of the sulphur. Nitrous acid derived from other sources, as from the action of nitric acid on organic matters, such as starch or sugar, in the manufacture of oxalic acid, or upon metals, is sometimes resorted to.) The process of its manufacture is generally conducted nearly as follows: the mixture of sulphur and nitre is burned in a furnace, so placed that the resulting fumes may pass into a capacious leaden chamber (frequently 100 feet long, 20 to 30 feet wide, and 10 to 16 feet high), the floor of which is covered with water, and into which steam is also generally introduced: in many works several of these chambers, or *houses*, as they are termed, are ranged side by side in covered buildings. The following cut will serve to give some idea of the internal construction of one of these houses: *a* is the furnace for the combustion of the sulphur and nitre, the fumes from which pass into the chamber and meet with the steam generated in the boiler *b*; the interior of the chamber is divided into several partitions, *c c*, by the

diaphragms *d d*, which are alternately open at top and bottom, so that the vapors pass in the direction of the darts, and are exposed to a large

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condensing surface. *e* is a chimney or ventilator. The water which collects in the bottom of this chamber gradually becomes more and more sour, and is, in fact, a diluted sulphuric acid; when it has thus acquired a certain specific gravity, 1·2 to 1·3, it is drawn off into shallow leaden boilers, where it is evaporated till it acquires the specific gravity of 1·70, at which density the acid would begin to act upon the lead, and the heat required for its further evaporation would endanger the softening of that metal; in this degree of concentration, therefore, the acid is run off into boilers, or rather into stills of platinum, which are set upon cast-iron, and in which the further boiling down of the acid is continued until it attains the specific gravity of 1·84; it is then drawn off by a syphon into a platinum cistern or cooler, and is thence transferred into *carboys*, or large bottles protected by basket-work, each holding about 100 pounds of the acid. Before the introduction of platinum vessels, the evaporation was finished in glass retorts, the lifting and emptying of which, when containing many pounds of the acid, was a very hazardous operation; the price of the acid fell, in consequence, from fourpence to about three-halfpence, or less, per pound, and at present the market price is a penny, or a fraction more than a penny, per pound. The manufacture of sulphuric acid is carried on upon a most extensive scale in Great Britain; the quantity annually produced probably not falling far short of sixty thousand tons, or about one hundred million of pounds, which, at the estimated value of ten shillings per cwt., amounts to above 600,000*l*. Though it is commonly called *sulphuric acid* (or oil of vitriol), it is in fact a definite combination of anhydrous sulphuric acid and water, composed of 1 atom of anhydrous acid + 1 atom water.

In the above process, the theory of which will be presently explained, the sulphurous acid is converted into sulphuric acid by the agency of nitric oxide and water. Other methods of forming sulphuric acid have been suggested, but not hitherto applied on a large scale; among them the following deserves particular notice: “When a mixture of sulphurous acid and air is made to pass over spongy platinum at a high temperature, the sulphurous acid is converted into sulphuric acid at the expense of the oxygen of the air. Mr. Phillips, who first made this observation, has founded upon it a proposal for preparing sulphuric acid on the large scale. Sulphur is burned, or iron pyrites in place of it, and the sulphurous acid produced is mixed with an excess of air by a blowing apparatus, and carried through a tube filled with the platinum sponge, or balls of fine platinum wire. The vapors of sulphuric acid formed which are mixed with the nitrogen of the air are condensed in a long and narrow vessel of lead in an upright position, filled with pebbles which are kept constantly wet

by a small stream of water admitted at the top, and which percolates downwards." (GRAHAM.)

A patent for making sulphuric acid without the aid of nitre, was taken some years ago by Mr. Hill. It consists in submitting coarsely-powdered iron pyrites (bisulphuret of iron) to a red heat, in cylinders communicating with a leaden chamber containing water; part of the sulphur, as it burns out of the pyrites, appears at once to pass into the state of sulphuric acid; with the help of nitre the pyrites might perhaps be more economically employed, but the arsenic which it is apt to contain is a strong objection to it.

The great consumers of sulphuric acid are the manufacturers of soda from common salt, and of chlorine or chloride of lime for the use of bleachers; there are also many other chemical products dependent upon it, such as citric, tartaric, acetic, nitric, and hydrochloric acids; sulphate of soda; sulphate of magnesia; and others of less note; it is also in constant demand by dyers, calico-printers, bleachers of various materials, the manufacturers of blacking, of soda-water, of various pigments, and by the refiners of gold and silver, and the purifiers of oil and tallow.

Sulphuric acid, or, as it ought more properly to be designated, *monohydrated sulphuric acid*, $\text{SO}_3\text{H}_2\text{O}$, is a limpid, inodorous, colorless fluid, of an oily consistence, and of the specific gravity of about 1.84. Dr. Ure observes that he has frequently boiled the pure acid till only one-half remained in the retort; yet at the temperature of 60° Fahrenheit, has never found the specific gravity of acid, so concentrated, to exceed 1.8455; the number 1.850, which has sometimes been assigned for the density of pure oil of vitriol, is therefore erroneous. Genuine *commercial* acid should never surpass 1.8455; when it is denser, we may infer sophistication, or negligence in the manufacture.

Sulphuric acid boils at a temperature of about 620° , which, therefore, approaches a red-heat, and distils over without decomposition. Its boiling-point diminishes with its dilution; when of the specific gravity of 1.78 it boils at 435° ; and at 350° , when its specific gravity is 1.65. (DALTON, *Chem. Phil.*, ii. 404.) In illustration of its fixedness at all common temperatures, Bellani placed a piece of zinc foil in the upper part of a closed bottle, the bottom of which was covered with the concentrated acid; the metal retained its bright surface at the end of two years. Berzelius, Vogel, and Wrede have assumed that oil of vitriol does give off vapor at common temperatures, and that therefore it cannot be employed in cases where extreme accuracy is required, as a means of drying air and gases; but Dumas has shown that in these cases the sulphuric acid was not perfectly free from sulphurous acid, and that a current of air passed first over potassa, and then through a tube of pumice moistened with sulphuric acid, has not the slightest effect when afterwards transmitted through a solution of chloride of barium. (*Ann. Ch. et Ph.*, Juin, 1843, p. 204.) The concentrated acid freezes at -15° ; and at the same time contracts considerably in its dimensions; acid of the specific gravity of 1.78 (which is a definite hydrate containing 1 atom of anhydrous sulphuric acid and 2 atoms of water,) on the contrary, freezes at $+40^\circ$, but if the density be either increased or diminished, a greater cold is required for its congelation. (MACNAB, *Phil. Trans.*, vol. LXXvii., and KEIR, *Phil. Trans.*, vol. LXXviii.)

Sulphuric acid is intensely acrid and caustic; it acts speedily upon the cuticle, occasioning a biting sensation, and a soapy feel of the part, in consequence of its chemical action on the cuticle: its taste, even when very largely diluted, is extremely sour, and it powerfully reddens litmus. It has a strong attraction for water, so that it absorbs aqueous vapor from the atmosphere and increases rapidly in bulk; in moist weather three parts increase to four in the course of 24 hours, and by longer exposure a larger quantity of water is taken up, so that it requires to be preserved in well-stopped vessels. It is this property which renders it applicable to the drying of certain gases, and to the purposes of evaporation and desiccation under the exhausted receiver of the air-pump, and hence the cold produced in Leslie's freezing experiment described at p. 83. When sulphuric acid is suddenly mixed with water, mutual condensation ensues, and much heat is evolved (p. 64). Four parts of acid, sp. gr. 1.8, and one of water at 32° , produce, when thus mixed, a temperature $= 212^{\circ}$. According to Dr. Ure, the greatest heat is evolved by mixing 73 of acid with 27 of water. Even a boiling temperature does not prevent sulphuric acid taking up moisture from the air; hence it cannot be concentrated so well in an open as in a close vessel; on which account retorts, or platinum stills, are used for the last stage of its concentration by the manufacturers. The mixture of sulphuric acid with ice or snow causes its immediate liquifaction, and as this liquifaction, consistently with the theory of latent heat, produces cold, while on the other hand the union of the acid with the water evolves heat, the resulting temperature of such mixture depends upon the relative proportions of the substances mixed. Four parts of acid and one of snow, or pounded ice, evolve heat; but four parts of snow and one of acid generate cold. When the acid of sp. gr. 1.78 ($\text{SO}_3, 2\text{HO}$), is mixed with snow, a great depression of temperature is the consequence; so that if to oil of vitriol, SO_3HO , such quantity of water be added as to convert it into $\text{SO}_3, 2\text{HO}$ heat is evolved, and then the further addition of snow occasions cold.

Sulphuric acid possesses intense chemical powers; under ordinary circumstances it displaces the greater number of other acids from their combinations; thus, in the humid way, it decomposes the phosphates and the borates; at a red heat, however, the phosphoric and the boracic acids which are comparatively fixed in the fire, expel sulphuric acid from its salts. A solution of sulphate of lime is decomposed by oxalic acid which forms an insoluble oxalate of lime, and the tartaric, racemic, and perchloric acids decompose sulphate of potassa in solution. In consequence, probably, of its strong affinity for water, sulphuric acid chars most organic substances; it acquires a brown tinge from the smallest particles of straw, cement, or dust, that accidentally fall into it; it appears capable of dissolving small portions of charcoal, and also of sulphur, tellurium, and selenium; these substances give it various tints of brown, red, and green, or blue, and are precipitated when the acid is diluted with water; but if heat be applied they are oxidized at the expense of the acid, and sulphurous acid is evolved.

When heated with charcoal, sulphuric acid gives rise to the production of carbonic and sulphurous acids ($\text{C} + 2\text{SO}_3 = \text{CO}_2 + 2\text{SO}_2$): with phosphorus it produces phosphoric and sulphurous acids, ($\text{P} + 5\text{SO}_3 = \text{PO}_5 + 5\text{SO}_2$) and, with sulphur, sulphurous acid is the only product, (S

+2SO₃=3SO₂.) It is decomposed by several of the metals, which become oxidized, and evolve sulphurous acid, as shown in the production of that acid by boiling sulphuric acid with mercury, tin, lead, &c. When metals are dissolved in *diluted* sulphuric acid, the water only is decomposed, and its oxygen, being transferred to the metal, forms a *metallic oxide*, which unites to the undecomposed sulphuric acid to form a *sulphate of the oxide*, whilst the hydrogen is evolved in the gaseous form.

It appears from Faraday's experiments (*Phil. Trans.*, 1834, p. 82), that sulphuric acid is not an electrolyte, and that the anhydrous acid is not a conductor. The appearance of sulphur, when the common acid is subjected to the action of a powerful battery, at the negative pole, is referable to a secondary action. But the electrolysis of hydrated sulphuric acid, and more especially of some of the sulphates, involves many interesting points respecting the ultimate constitution of those bodies, which we shall again refer to under the head of *sulphate of ammonia*, and also when considering the *salts of the metals*. (DANIELL, *Phil. Trans.*, 1839, p. 89; 1840, p. 209.)

The presence of sulphuric acid, either free or in any soluble combination, is detected by solution of baryta; if, for instance, a solution of chloride of barium be added to any liquid containing sulphuric acid or a sulphate, a white precipitate falls, which is *sulphate of baryta*, and is characterized by its insolubility in acids and alkalis. 117 parts of dry sulphate of baryta are equivalent to 40 of dry sulphuric acid, and to 49 of oil of vitriol. The soluble salts of lead are also delicate tests of the presence of sulphuric acid: they indicate it by a white precipitate, insoluble in nitric acid. When this precipitate is collected, washed, and perfectly dried, 152 parts of it by weight are equivalent to 40 of anhydrous sulphuric acid. (See the articles *sulphate of baryta* and *sulphate of lead* in reference to the peculiarities of their precipitates.)

In consequence of the great consumption of sulphuric acid, and the numerous arts and manufactures in which it is in constant use, it is important to the consumer to be able to judge of its value and purity; the *specific gravity* may generally be depended upon as indicative of its *strength*, and we have several valuable tables showing the quantity of real or dry sulphuric acid contained in the liquid or diluted acid of various specific gravities. Dalton (*New System of Chemical Philosophy*, vol. ii. p. 404) has published a table, exhibiting the specific gravity and boiling-point of the acid, of various strengths. Ure has also given tables relating to this subject, in his *Experiments to determine the Law of Progression followed in the Density of Sulphuric Acid at different Degrees of Dilution*. (*Quarterly Journal of Science and the Arts*, vol. iv. p. 114.) An extremely useful table of this kind will also be found in PARKES' *Essays*, (2nd Edit. i. 504): but upon the whole, Dr. Ure's table appears to be the most correct, as it is also the most extensive. For the use of the manufacturer and of the chemical laboratory, glass hydrometers are made for the express purpose of determining the specific gravity of the commercial oil of vitriol, and they are very convenient where minute accuracy is not required, and where the absence of saline impurities has been previously ascertained. But where the specific gravity of the acid is to be more accurately determined, the usual mode by weighing must be resorted to, as described in a former chapter. (See page 43.)

The following is Dr. Ure's table:

Liq.	Sp. Gr.	Dry.	Liq.	Sp. Gr.	Dry.	Liq.	Sp. Gr.	Dry.
100	1·8485	81·54	66	1·5503	53·82	32	1·2334	26·09
99	1·8475	80·72	65	1·5390	53·00	31	1·2260	25·28
98	1·8460	79·90	64	1·5280	52·18	30	1·2184	24·46
97	1·8439	79·09	63	1·5170	51·37	29	1·2108	23·65
96	1·8410	78·28	62	1·5066	50·55	28	1·2032	22·83
95	1·8376	77·46	61	1·4960	49·74	27	1·1956	22·01
94	1·8336	76·65	60	1·4860	48·92	26	1·1876	21·20
93	1·8290	75·83	59	1·4760	48·11	25	1·1792	20·38
92	1·8233	75·02	58	1·4660	47·29	24	1·1706	19·57
91	1·8179	74·20	57	1·4560	46·48	23	1·1626	18·75
90	1·8115	73·39	56	1·4460	45·66	22	1·1549	17·94
89	1·8043	72·57	55	1·4360	44·85	21	1·1480	17·12
88	1·7962	71·75	54	1·4265	44·03	20	1·1410	16·31
87	1·7870	70·94	53	1·4170	43·22	19	1·1330	15·49
86	1·7774	70·12	52	1·4073	42·40	18	1·1246	14·68
85	1·7673	69·31	51	1·3977	41·58	17	1·1165	13·86
84	1·7570	68·49	50	1·3884	40·77	16	1·1090	13·05
83	1·7465	67·68	49	1·3788	39·95	15	1·1019	12·23
82	1·7360	66·86	48	1·3697	39·14	14	1·0953	11·41
81	1·7245	66·05	47	1·3612	38·32	13	1·0887	10·60
80	1·7100	65·23	46	1·3530	37·51	12	1·0809	9·78
79	1·6993	64·42	45	1·3440	36·69	11	1·0743	8·97
78	1·6870	63·60	44	1·3345	35·88	10	1·0682	8·15
77	1·6750	62·78	43	1·3255	35·06	9	1·0614	7·34
76	1·6630	61·97	42	1·3165	34·25	8	1·0544	6·52
75	1·6520	61·15	41	1·3080	33·43	7	1·0477	5·71
74	1·6415	60·34	40	1·2999	32·61	6	1·0405	4·89
73	1·6321	59·52	39	1·2913	31·80	5	1·0336	4·08
72	1·6204	58·71	38	1·2826	30·98	4	1·0268	3·26
71	1·6090	57·89	37	1·2740	30·17	3	1·0206	2·446
70	1·5975	57·08	36	1·2654	29·35	2	1·0140	1·63
69	1·5868	56·26	35	1·2572	28·54	1	1·0074	0·8154
68	1·5760	55·45	34	1·2490	27·72			
67	1·5648	54·63	33	1·2409	26·91			

In ascertaining the specific gravity of sulphuric acid, the *temperature* requires minute attention, because from the small specific heat of the acid it is easily affected, and because it greatly influences the density. On removing the thermometer from the acid, it speedily rises in the air to 75° or 80° , though the temperature of the apartment be only 60° ; afterwards it slowly falls to 60° . If this thermometer, having its bulb covered with a film of dilute acid (from absorbing atmospheric moisture), be plunged into a strong acid, it will rise 10° or more, and an elevation equal to 10° diminishes the density of oil of vitriol by 0·005; 1000 parts being heated from 60° to 212° , become 1043 in volume, and the sp. gr. which was 1·848, falls to 1·772, being the number corresponding to a dilution of 14 per cent. of water.

But it is also necessary to ascertain that the sulphuric acid under examination leaves no residue on evaporation. If the acid of commerce contain dissolved sulphate of lead, it becomes turbid on dilution, so that its remaining clear when mixed with water is some proof of its purity, as far at least as lead is concerned. The simplest mode of judging of the freedom of this acid from fixed impurities, is to introduce a given weight into a platinum capsule and evaporate it; if it leaves more than one *per cent.* of solid residue, it has probably been intentionally sophisticated.

It often holds sulphate of potassa in solution, 2·5 per cent. of which increases the specific gravity of the concentrated acid to 1·860; hence the necessity, where accuracy is required, of determining the value of the acid by its *saturating power*. For this purpose, a given weight of the acid is diluted with six or eight parts of water, and a solution (of known strength) of pure carbonate of soda added until the solution is exactly neutral (see *Alcalimetry*). Every 54 parts of anhydrous carbonate of soda are equivalent to 40 parts of the anhydrous acid, or to 49 of the liquid sulphuric acid, or oil of vitriol, of the specific gravity of 1·84. Besides lead and potassa, tin and arsenic are sometimes found in sulphuric acid: the former arising from the solder of the leaden chambers, and the latter derived from the sulphur or pyrites. The modes of detecting these impurities will be stated under the respective metals. According to Dupasquier (*Phil. Mag.*, Oct. 1843), sulphuretted hydrogen fails to detect the sulphate of lead dissolved in or mixed with excess of sulphuric acid, but when the contaminated acid is saturated by an alkaline base, the test becomes efficient and forms black sulphuret of lead.

Dr. Ure has the following remarks on the distillation of this acid:—“I take a plain glass retort, capable of holding from two to four quarts of water, and put into it about a pint measure of sulphuric acid, (and a few fragments of glass,) connecting the retort with a large globular receiver, by means of a glass tube four feet long, and from one to two inches in diameter. The tube fits very loosely at both ends. The retort is placed over a charcoal fire, and the flame is made to play gently on its bottom. When the acid begins to boil smartly, sudden explosions of dense vapor rush forth from time to time, which would infallibly break small vessels. Here, however, these expansions are safely permitted, by the large capacity of the retort and receiver, as well as by the easy communication with the air at both ends of the adapter tube. Should the retort, indeed, be exposed to a great intensity of flame, the vapor will no doubt be generated with incoercible rapidity, and break the apparatus; but this accident can proceed only from gross imprudence. It resembles in suddenness the explosion of gunpowder, and illustrates admirably Dr. Black's observation, that, but for the great latent heat of steam, a mass of water, powerfully heated, would explode on reaching the boiling temperature. I have ascertained, that the specific caloric of the vapor of sulphuric acid is very small, and hence the danger to which rash operators may be exposed during its distillation. Hence, also, it is unnecessary to surround the receiver with cold water, as when alcohol and most other liquids are distilled. Indeed the application of cold to the bottom of the receiver generally causes it, in the present operation, to crack. By the above method, I have made the concentrated oil of vitriol flow over in a continuous slender stream, without the globe becoming sensibly hot.” The sudden explosions of vapor which Dr. Ure here refers to are probably connected with the adhesion of the acid to the glass, and come under the phenomena investigated by Donny (see p. 310).

As common sulphuric acid contains traces of nitrous and hyponitrous acid, a little sulphur is generally added, previous to distillation, for the purpose of their decomposition; but this gives rise to sulphurous acid, which is retained even after repeated distillations: to deprive it of this latter acid, Jacquelin (*Ann. Ch. et Ph.*, Feb. 1843), recommends adding to the

acid already distilled with sulphur a little aqueous chlorine, and afterwards boiling a few minutes. After these operations, it no longer retains nitric, sulphurous, or hydrochloric acids. The presence of nitric or nitrous acid is indicated in sulphuric acid by the discoloration occasioned by adding a few drops of concentrated solution of protosulphate of iron: a solution of narcotine is also reddened by sulphuric acid containing nitrous acid. With the iron test the color after a time becomes paler, but with the narcotine test deeper; but the iron test is preferable, inasmuch as *pure* sulphuric acid is to a certain extent discolored by narcotine.

Cases of poisoning by sulphuric acid are not unfrequent; the best antidotes are copious draughts of chalk or whiting and water, or of carbonate of magnesia and water. (TAYLOR. *Med. Jurisp.* 91.)

Native Sulphuric Acid has been found by Professor Baldassari, in the cavities of a small volcanic hill, called Zoccolino, near Sienna. It is probably not uncommon in similar situations.

ANHYDROUS SULPHURIC ACID. When crystallized green vitriol, or protosulphate of iron, is exposed to a dull red-heat, it crumbles down into a white powder, and loses the greater part of its water of crystallization. (See *Sulphate of Iron*.) In this state, if put into a coated earthen or green glass retort, and gradually exposed to an intense red or even white heat, a dark-colored liquor distils over, of a specific gravity of about 1.89, which has been called *Nordhausen*, or *German sulphuric acid*; it smokes when exposed to air, from the escape of the highly volatile *dry* sulphuric acid, which is united in the brown liquid with a portion of hydrated acid. The brown, fuming acid, is in request as a ready and perfect solvent of indigo. When it is kept at a temperature below 32°, crystals form in it, which according to Mitscherlich are a definite compound of 2 atoms of anhydrous acid and 1 atom of water; it is resolved by heat into the common and the anhydrous acid.

The dry or *anhydrous sulphuric acid* may be separated from this brown (or *Nordhausen*) acid, by careful distillation from a retort into a dry and cold receiver; it passes over in drops, which concrete, on cooling, into a tenacious crystalline mass. This acid is liquid at a temperature above 66°; and at 78° its specific gravity, according to Bussy, is 1.97. (*Journal de Pharmacie*, x. 368.) When it has once congealed it is difficult to fuse it, because the first portions heated become vapor, and propel the rest forward; by slight pressure, however, this may be prevented. When kept in a temperature between 75° and 80°, it gradually liquifies. At a temperature somewhat above this, which, however, has not been accurately determined, it passes into the state of colorless vapor, the density of which, according to Mitscherlich, is 3. The calculated density is 2.77, so that 100 cubic inches would weigh 85.969 grains. In the absence of all moisture, it has no action upon litmus paper. Passed through a red-hot porcelain tube, anhydrous sulphuric acid is resolved into *one volume of oxygen and two of sulphurous acid*. Caustic lime or baryta heated in its vapor, become ignited, and converted into sulphates. The attraction of this anhydrous acid for water is such as to produce intense heat and a hissing noise when small portions of it are thrown into that fluid; and if a sufficient quantity of it be added to such a proportion of water as is required to convert it into hydrated acid, they combine with heat, light, and explosion.

The brown and fuming liquid acid, from sulphate of iron, yields about one-fourth its weight of anhydrous acid by distillation; but if this cannot be procured, the anhydrous acid may be obtained, according to Berzelius, by the distillation of such other sulphates as easily part with their acid: those sulphates which require a very elevated temperature, are less fit for the purpose, because the acid is then apt to be resolved into sulphurous acid and oxygen. Bisulphate of soda, or persulphate of iron, may thus be employed. The former may be made by mixing in a crucible three parts of thoroughly-desiccated sulphate of soda with two of common sulphuric acid, and heating them till the ebullition occasioned by the escape of water has ceased. The resulting mass is then to be pulverized, transferred to a porcelain retort, and distilled at a red heat; the acid which passes over may be collected in a receiver cooled by ice: it is generally of a dark color, which appears to arise from dust accidentally present. A persulphate of iron, applicable to the same purpose, may be procured by mixing finely-powdered peroxide of iron into a thin paste with common sulphuric acid, and gradually heating it (below redness) till they combine into a saline mass, which is to be powdered and subjected to distillation as before. The acid thus obtained generally contains a little water, and if it crystallizes, it forms brittle foliaceous crystals. Carefully redistilled by a gentle heat, the anhydrous acid passes over, and common liquid acid (hydrated) remains in the retort.

It appears, then, that this extraordinary substance, which is thus volatile and easy of congelation, forms, by combining with water, the fixed and difficultly-congealable *oil of vitriol*, and that it contains sulphur and oxygen in the same proportions as they exist in the acid of the dry sulphates. From its resolution when passed through a red-hot tube, into one volume of sulphurous acid and half a volume of oxygen, and likewise from the experiments of Berzelius upon the direct acidification of sulphur, it appears that *anhydrous sulphuric acid* consists of

				Berzelius.
Sulphur	1	16	40	40.14
Oxygen	3	24	60	59.86
<hr/>				
Anhydrous sulphuric acid.....	1	40	100	100.00

And the *liquid, hydrous, or common sulphuric acid, or oil of vitriol*, when of the sp. gr. 1.845 consists of

					Davy and Dalton.		
Dry sulphuric acid	1	...	40	...	81.63	...	81
Water	1	...	9	...	18.37	...	19
<hr/>							
Monohydrated sulphuric acid	1		49		100.00		100

The compound of sulphuric acid and water of the specific gravity 1.78, which has been above alluded to as congealing at 40° , remains solid till raised to 45° , and is a definite combination of 1 atom of anhydrous acid + 2 atoms of water; and lastly, the acid of specific gravity 1.632 appears also to be a definite hydrate containing 1 atom of anhydrous acid and 3 atoms of water, for it is to this strength that a dilute sulphuric acid evaporated in vacuo at 212° is reduced, and it is also in these proportions that sulphuric acid and water suffer the greatest diminution of bulk in combining. It would appear, therefore, that there are

four definite hydrates of sulphuric acid; of which the following are the formulæ :

Anhydrous acid	SO ₃
Hydrate in the Nordhausen acid	2 SO ₃ ,HO
Oil of vitriol, sp. gr. 1·845.....	SO ₃ ,HO
Acid of sp. gr. 1·780	SO ₃ ,2HO
Acid of sp. gr. 1·632	SO ₃ ,3HO

Graham, in reference to the composition of the *sulphates*, arranges these formulæ as follows :

Hydrate in the Nordhausen acid	HO,2SO ₃
Oil of vitriol.....	HO,SO ₃
Acid of sp. gr. 1·780.....	HO,SO ₃ + HO
Acid of sp. gr. 1·632.	HO,SO ₃ + 2HO

THEORY OF THE PRODUCTION OF SULPHURIC ACID. Having stated the properties and composition of sulphuric acid, we may now revert to the *theory of its formation* in the process of the combustion of sulphur and nitre. It was first supposed that the nitre merely yielded oxygen directly to the sulphur, and so effected its perfect acidification ; but the small quantity of nitre required, and the production of sulphurous and not sulphuric acid, when sulphur is either burned alone in pure oxygen gas, or when it is heated with peroxide of manganese and other substances which readily impart oxygen, seemed to indicate some other power possessed by the nitre ; that this is the case was proved by Clément and Désormes (*Ann. de Chim.*, LIX.) and by Davy (*Elements of Chem. Philos.*, 276), to whom we owe the following explanation of the phenomena.

The sulphur by burning in contact with atmospheric air forms *sulphurous acid* ; the nitre is at the same time decomposed, and yields *nitrous acid*. When these vapors (*i. e.*, sulphurous and nitrous acids) are *perfectly dry*, they do not act upon each other, but moisture being present in small quantity, they form a white solid, which is instantly decomposed by the contact of water ; the nitrous acid reverts to the state of nitric oxide, having transferred one additional proportional of oxygen to the sulphurous acid, and, with water, producing the sulphuric acid ; while the nitric oxide, by the action of the air, again affords nitrous acid, which plays the same part as before. ($2\text{SO}_2 + \text{NO}_4 + 2\text{HO} = 2[\text{SO}_3, \text{HO}] + \text{NO}_2$.) The following diagrams (omitting water) represent the changes more in detail :

Sulphurous acid consists of

Sulphur.	
16	Oxygen. 8
	8
} 16 + 16 = 32	

And nitrous acid contains

Nitrogen.	
	Oxygen. 8
14	8
	8
	8
} 32 + 14 = 46	

Hence every *two* proportionals of sulphurous acid require *one* of nitrous

acid, which transfers *two* of oxygen, and passes back into the state of nitric oxide, sulphuric acid being, at the same time, produced.

The gases, therefore, before decomposition, may be thus represented:

Sulphur.		
16	Oxygen. 8	} 16
Sulphur.	8	
16	8	} 16
	8	
Two proportionals of Sulphurous Acid.		

Nitrogen.	Oxygen. 8	} 32
14	8	
	8	
	8	
One proportional of Nitrous Acid.		

And after decomposition as follows:—

Sulphur.			
16	Oxygen. 8	}	24
	8		
Sulphur.	8	}	24
	8		
16	Oxygen. 8	}	24
	8		
	8	}	24
	8		
Two proportionals of Sulphuric Acid.			

Nitrogen.	Oxygen. 8	}	16
14	8		
One proportional of Nitric Oxide.			

Or if it be assumed that the compound upon which the formation of sulphuric acid depends, is one of hyponitrous and sulphurous acid; then $\text{SO}_2 + \text{NO}_3 + \text{HO} = \text{SO}_3\text{HO} + \text{NO}_2$.

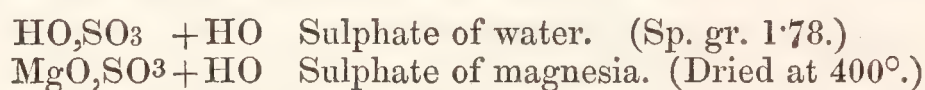
The theory of the production of sulphuric acid has more lately engaged the attention of Peligot, (*Ann. Ch. et Ph.*, November, 1844,) whose paper contains an account of the mutual reactions of sulphurous and nitric acids at different temperatures; the formation of sulphuric acid, he observes, depends upon the following facts: 1. Sulphurous acid decomposes nitric acid, forming sulphuric and nitrous acids. 2. Water changes the nitrous into nitric and hyponitrous acid. 3. The hyponitrous acid under the influence of more water, becomes nitric acid and binoxide of nitrogen. 4. The binoxide of nitrogen in contact of air, produces nitrous acid, which is, 5. transformed by water into hyponitrous and nitric acid. The sulphurous acid acts incessantly and exclusively on the nitric acid, constantly regenerated in the different phases of the operation; this series of successive reactions exclude the intervention

of any crystallizable compound, and are represented in the following formulæ*:

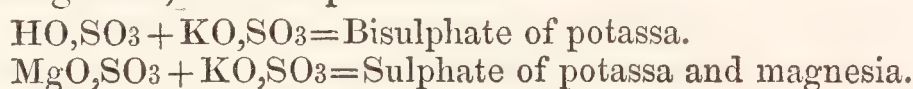
1. $\text{NO}_5, \text{HO} + \text{SO}_2 = \text{SO}_3, \text{HO} + \text{NO}_4$
2. $2\text{NO}_4 + \text{HO} = \text{NO}_3 + \text{NO}_5, \text{HO}$
3. $3\text{NO}_3 + \text{HO} = 2\text{NO}_2 + \text{NO}_5, \text{HO}$
4. $\text{NO}_2 + 2\text{O} = \text{NO}_4$
5. $2\text{NO}_4 + \text{HO} = \text{NO}_3 + \text{NO}_5, \text{HO}, \text{ \&c.}$

SULPHATES. In the neutral anhydrous sulphates the water of the oil of vitriol is replaced by a metallic oxide; so that instead of $\text{HO} + \text{SO}_3$, we have $\text{MO} + \text{SO}_3$. But if oil of vitriol be viewed as a hydracid, $= \text{H} + \text{SO}_4$, the hydrogen may then be regarded as replaced by the metal, giving $\text{M} + \text{SO}_4$.

Graham observes, that many of the sulphates (especially those of the magnesian family,) correspond with the binhydrate of sulphuric acid (sp. gr. 1.78). Thus, of the 7 atoms of water in crystallized sulphate of magnesia, it retains 1 at 400° . So that we have



The atom of water may be replaced in both these salts by an atom of sulphate of potassa, in which case *bisulphate of potassa*, and *sulphate of potassa and magnesia*, are the products.



On the binary theory, the sulphates are compounds of metals, with SO_4 ; sulphate of potassa, for instance, being K, SO_4 , instead of KO, SO_3 .

If the different acids of sulphur, in their isolated state, be regarded as including an atom of water, the salts of the same acids will be formed by the substitution of an atom of metallic oxide for that of water: or if, on the binary theory, the same acids be regarded as hydracids, or as compounds of hydrogen, then the replacement of that hydrogen by a metal will form the corresponding salt: Dr. Gregory gives the following table in illustration of these views:

	OLD VIEW.		NEW VIEW.	
	Acids.	Salts.	Acids.	Salts.
Sulphurous acid	HO, SO_2	MO, SO_2	H, SO_3	M, SO_3
Sulphuric acid	HO, SO_3	MO, SO_3	H, SO_4	M, SO_4
Hyposulphurous acid	$\text{HO}, \text{S}_2\text{O}_2$	$\text{MO}, \text{S}_2\text{O}_2$	$\text{H}, \text{S}_2\text{O}_3$	$\text{M}, \text{S}_2\text{O}_3$
Hyposulphuric acid	$\text{HO}, \text{S}_2\text{O}_5$	$\text{MO}, \text{S}_2\text{O}_5$	$\text{H}, \text{S}_2\text{O}_6$	$\text{M}, \text{S}_2\text{O}_6$
Acid of Langlois	$\text{HO}, \text{S}_3\text{O}_5$	$\text{MO}, \text{S}_3\text{O}_5$	$\text{H}, \text{S}_3\text{O}_6$	$\text{M}, \text{S}_3\text{O}_6$
Acid of Fordos and Gélis....	$\text{HO}, \text{S}_4\text{O}_5$	$\text{MO}, \text{S}_4\text{O}_5$	$\text{H}, \text{S}_4\text{O}_6$	$\text{M}, \text{S}_4\text{O}_6$

He advocates the new view, or binary theory, on account of its simplicity: according to it, *an acid* may be defined as a combination of hydrogen, with a radical either simple or compound, in which the hydrogen may be replaced by its equivalent of metal; while *a salt* is a combination of a simple or compound radical, with a metal. One obvious advantage of this binary theory is, that it assimilates the salts of the oxyacids with those of the hydracids, and so far simplifies the chemistry of the salts in general.

* Our hyponitrous acid is the *acide nitreux* of the author; and our nitrous acid, is his *acide hyponitrique*.

SULPHURIC ACID AND NITRIC OXIDE. NO_2 , 2SO_3 . Dry nitric oxide is absorbed by anhydrous sulphuric acid. (H. ROSE.) When liquified sulphurous and nitrous acids are brought together in a sealed glass tube, heat is evolved, and the mixture gradually deposits a yellowish crystalline matter, which in 24 hours amounts to about 0·9 of the mixture, while 0·1 of a greenish fluid separates, which evaporates with explosive violence on opening the tube. ($\text{NO}_4 + 2\text{SO}_2 = \text{NO}_2, 2\text{SO}_3$.) Provostaye (*Ann. Ch. et Ph.*, LXXIII. 362,) regards the green fluid as hyponitrous acid; but its extreme explosive violence renders its further examination desirable. The solid portion yields, after fusion, a white mass of acicular crystals and prisms of the sp. gr. 2·14, fusible at about 430° , and congealing at 420° ; at these temperatures it is yellow and transparent, till cooled to 375° ; below this it becomes opaque and greenish, but white when cool. It may be distilled without decomposition, at about 620° . It dissolves rapidly in water, forming a solution of sulphuric acid and evolving nitric oxide. It dissolves in warm sulphuric acid (protohydrated), and on cooling yields a crystalline mass. The real nature of the crystalline compounds resulting from the action of sulphurous and sulphuric acids upon the nitrous and nitric acid is still involved in much doubt.

SULPHURIC ACID AND AMMONIA. SULPHATE OF AMMONIA. GLAUBER'S SECRET SAL-AMMONIAC. SULPHATE OF OXIDE OF AMMONIUM. NH_3 , SO_3 , HO , or NH_4O , SO_3 . This salt may be obtained directly by pouring a few drops of sulphuric acid into a bottle of gaseous ammonia; the ammonia is rapidly absorbed, and the salt crystallizes on the sides of the jar. It is usually prepared by saturating dilute sulphuric acid with carbonate of ammonia. It is important as a source of *sal ammoniac*, which is obtained by sublimation from a mixture of chloride of sodium and sulphate of ammonia; by this process sulphate of soda is also formed. (NH_4O , $\text{SO}_3 + \text{NaCl} = \text{NH}_4\text{Cl} + \text{NaO}$, SO_3 .) (See *Sodium*.) For these purposes the *ammoniacal liquor* of gas-works, produced during the destructive distillation of coal, and the impure carbonates of ammonia formed by the distillation of bones and other refuse animal matters, are saturated by sulphuric acid, and the resulting sulphate of ammonia purified by crystallization.

Sulphate of ammonia, in its common form of six-sided prismatic crystals, contains, according to Berzelius, two proportionals of water, being composed of

						Berzelius.
Ammonia	1	17	22·7 22·6
Sulphuric acid	1	40	53·3 53·1
Water	2	18	24·0 24·3
<hr/>						<hr/>
Crystallized sulphate of } ammonia	1		75		100·0	100·0

It is soluble in two parts of water at 60° and in one at 212° . Its taste is bitter and pungent. When heated, it melts and in part sublimes, ammonia is given off, and a *bi-sulphate* remains, containing 2 proportionals of acid + 1 of ammonia: at a higher temperature, nitrogen and water are given out, and sulphite of ammonia (or probably sulfimide) is formed.

Sulphate of ammonia has lately been much used as a manure, and is

largely manufactured for this purpose. (See JOHNSTON'S *Lectures on Agricultural Chemistry*, &c. Appendix, 56, 80.)

To assimilate the composition of this salt with the other sulphates, it is assumed to be a *sulphate of oxide of ammonium*; it cannot exist without the atom of water belonging to the sulphuric acid, and is not formed, as we shall presently find, by the mutual action of ammonia and anhydrous sulphuric acid; upon this (hypothetical) view therefore of its constitution, ammonia becomes converted into ammonium by uniting to the hydrogen of the water in the acid, and the oxygen of this water converts the ammonium into oxide of ammonium, and this, combined with the anhydrous sulphuric acid, forms a sulphate of oxide of ammonium: it is evident that the elements of this hypothetical anhydrous sulphate of oxide of ammonium are equivalent to those of the hydrated sulphate of ammonia; for



But the electrolytic decomposition of a solution of sulphate of ammonia, the phenomena of which have been described by Daniell, (*Phil. Trans.*, 1839, p. 111,) furnishes another view of the constitution of this and other sulphates, which on many accounts is important in its theoretical bearings. Mr. Daniell found that hydrated sulphate of ammonia = $\text{NH}_3, \text{SO}_3, \text{HO}$, is resolved by electrolysis into 1 equivalent of sulphur and 4 of oxygen, given off at the anelectrode, and into 1 equivalent of nitrogen and 4 equivalents of hydrogen, given off at the cathelectrode; so that its electrolytic formula would be $\text{NH}_4, + \text{SO}_4$; thus representing it, not as a sulphate of oxide of ammonium, but as a compound of ammonium (NH_4) with a peculiar anion composed of 1 equivalent of sulphur and 4 of oxygen (SO_4). Such an anion Mr. Daniell provisionally designates *oxysulphion*; and hence the common sulphate of ammonia he terms *oxysulphion of ammonium*.

NATIVE SULPHATE OF AMMONIA is sometimes found in volcanic products; it occurs in stalactitic concretions of a whitish or yellowish color, and covered with a white efflorescence: it has thus been procured from fissures in the earth surrounding certain small lakes in Tuscany, near Sienna; and among the products of Etna and Vesuvius; it has been termed by Karsten, *Mascagnine*, from the name of its discoverer.

ANHYDROUS SULPHURIC ACID AND AMMONIA. Sulfamide. The principal evidence in favor of the above view of the constitution of the sulphate of ammonia is derived from *the action of anhydrous sulphuric acid on ammonia*. By conducting dry gaseous ammonia into a glass vessel coated with a thin film of anhydrous sulphuric acid, Rose obtained a crystallized compound, differing in form from sulphate of ammonia, and in which neither sulphuric acid nor ammonia are evident to the usual tests, although their elements must manifestly be included in the compound. (*Poggend.*, xxii., xlvii., and xlix.) It seems probable, therefore, that it may be an *amide* (a hydrated sulfamide), for the elements



HYPOSULPHUROUS ACID. DITHIONOUS ACID. S_2O_2 , or $SO_2 + S$. The existence of an acid compound of sulphur and oxygen, containing *one* atom of sulphur and *one* of oxygen ($16 + 8 = 24$), was first inferred by Dr. Thomson, in 1817, and the salts containing such a combination were originally described by Gay Lussac (*Ann de Chim.*, LXXXV.), under the name of *sulphuretted sulphites*. Higgins (*Comparative View*, p. 49) and Berthollet had previously found that iron and zinc might be dissolved in aqueous sulphurous acid, without any evolution of hydrogen gas, and that they formed peculiar colorless crystallizable salts, which, acted upon by certain other acids, evolved sulphurous acid and sulphur. By exposing sulphuret of sodium in solution to the air, Vauquelin obtained an analogous compound of soda. Thomson first suggested the term *hyposulphurous* for the peculiar acid of sulphur contained in these compounds, (*Syst. of Chem.*, 1817), and they were afterwards examined with much precision and ability by Herschel. (*Edin. Phil. Jour.*, i.) This acid has not been examined in a separate state, though Berzelius has suggested the probability of its existence in some of those peculiar colored compounds of anhydrous sulphuric acid and sulphur, which have been above adverted to. When we attempt to decompose its compounds in the humid way, sulphurous acid escapes, and sulphur is precipitated. By adding slight excess of sulphuric acid to a dilute solution of hyposulphite of strontia, Sir John Herschel succeeded in separating the acid, but it almost immediately began to undergo spontaneous decomposition, and was resolved into sulphurous acid and sulphur by heat. S_2O_2 becoming S and SO_2 .

Hyposulphurous acid is formed, 1. When sulphur is digested, at a high temperature but without ebullition, in a solution of a sulphite: in which case the oxygen of the sulphurous acid divides itself between the original and the newly added sulphur: thus we obtain hyposulphite of soda by digesting finely divided sulphur in a hot solution of sulphite of soda, $NaO, SO_2, + S$, becoming NaO, S_2O_2 . 2. When sulphurous acid gas is passed through a solution of an alkaline sulphuret till it no longer precipitates sulphur; thus, we obtain hyposulphite of lime by passing sulphurous acid gas through a solution of sulphuret of calcium; in which case $2 CaS$, and $3 SO_2$ become $2 CaO, 2 S_2O_2$, and S. 3. When a solution of an alkaline sulphuret (containing 2 or more atoms of sulphur) is exposed to air till it becomes nearly colorless, oxygen is slowly absorbed, and a hyposulphite results; thus one equivalent of bisulphuret of potassium would absorb three of oxygen, and form one of hyposulphite of potassa. $KS_2 + O_3 = KO, S_2O_2$. 4. When zinc or iron are digested in aqueous solution of sulphurous acid, a sulphite and hyposulphite of the metal is formed: thus 2 atoms of zinc and 3 atoms of sulphurous acid form 1 atom of sulphite and 1 atom of hyposulphite of oxide of zinc. $2 Zn + 3 SO_2 = ZnO, SO_2$, and ZnO, S_2O_2 .

It has been shown by Rose (*Poggendorff's Annalen*, xxi.), that although the ratio of the sulphur to the oxygen, in this acid, is as 16 to 8, its *equivalent*, or combining proportion, is not 24, but 48, hence it must be considered as a compound of

Sulphur	2	32	66·67	} = {	Sulphur	1	16	33·33
Oxygen	2	16	33·33		Sulphurous acid	1	32	66·67
<hr/>					<hr/>			
Hyposulphurous acid	1	48	100·00		1	48	100·00	

The *hyposulphites* are mostly soluble and of a bitter taste: the solutions of the alkaline hyposulphites occasion black precipitates in the nitrates of silver and mercury, which are *sulphurets*: the hyposulphites of lead and of baryta are thrown down in the form of white insoluble powders: the neutral hyposulphites dissolve recently-precipitated chloride of silver, and form with it a compound of a very sweet taste.

HYPOSULPHURIC ACID. DITHIONIC ACID. S_2O_5 . was discovered in 1819 by Gay Lussac and Welter. It was accidentally formed in an attempt to analyze oxide of manganese by the employment of sulphurous acid, when a peculiar salt was formed, which did not precipitate baryta. This salt was afterwards found to contain a distinct acid of sulphur, to which Gay Lussac gave the above name. (*Ann. Ch. et Ph.*, x.) It is obtained by passing a current of sulphurous acid through a cold mixture of finely-powdered and pure peroxide of manganese and water. A solution is obtained, which is filtered and thoroughly agitated and digested with hydrated baryta, which must be added in small excess. The sulphuric acid and the greater part of the oxide of manganese are thus precipitated. The solution is again filtered and evaporated till it crystallizes, and the crystals of *hyposulphate of baryta* are a second time dissolved and obtained by evaporation, in order to procure them free from manganese; they are then dried, powdered, weighed, and dissolved in water; and to every hundred parts of the dissolved salt, 18·78 parts of sulphuric acid, of the specific gravity of 1·84, diluted with four parts of water, are added. The baryta is thus thrown down in the state of sulphate, and the new acid remains in solution. Having been filtered, it is to be concentrated by exposure under the exhausted receiver of the air-pump, including a vessel of sulphuric acid, till it acquires the density of 1·347. If its exposure and evaporation be continued beyond this point, it is resolved into sulphuric and sulphurous acids. A temperature of 212° effects the same change in its composition. It is inodorous, sour, and reddens vegetable blues. It has not been obtained in an anhydrous state.

Neither oxygen, nor chlorine, nor nitric acid, nor peroxide of manganese, affect the composition of hyposulphuric acid at common temperatures; it dissolves zinc with the evolution of hydrogen, and hyposulphate of zinc results. It saturates the salifiable bases; and with lime, baryta, strontia, and protoxide of lead, it forms *soluble* compounds; whereas those formed by these bases with the sulphuric acid, are difficultly soluble or insoluble. Its salts, however, are not permanent at high temperatures, but when heated they are resolved into sulphates, with the escape of sulphurous acid; notwithstanding this, they remain *neutral*, though the quantity of sulphurous acid which escapes is such as would itself have saturated the base. The elements of this acid are in the relative proportions of 1 atom of sulphur and 2·5 oxygen, but its equivalent is not 36, but 72, hence it is constituted of

Sulphur	2	32	44·44	} = {	Sulphurous acid	1	32	44·44
Oxygen	5	40	55·56		Sulphuric acid.....	1	40	55·56
<hr/>					<hr/>			
Hyposulphuric acid	1	72	100·00		1	72	100·00	

SULPHURETTED HYPOSULPHURIC ACID. TRITHIONIC ACID. S_3O_5 . The existence of an acid having the preceding formula has been announced by

Langlois, as formed along with hyposulphates by digesting sulphur in a solution of bisulphite of potassa (see *Hyposulphite of Potassa*;) thus 3 atoms of bisulphite of potassa and 2 of sulphur, would produce 2 atoms of sulphuretted hyposulphate and 1 of hyposulphite; as in the following equation



The elements of an atom of the sulphuretted hyposulphuric acid are, as the following table shows, equivalent to those of an atom of hyposulphurous and an atom of sulphuric acid :

			Langlois.						
Sulphur	3	48	54·55	}	=	Hyposulphurous acid	1	48	54·55
Oxygen	5	40	45·45			Sulphuric acid	1	40	45·45
<hr/>			<hr/>			<hr/>			
Sulphuretted hypo- sulphuric acid	1	88	100·00				1	88	100·00

It neither precipitates the salts of baryta nor lead. (*Ann. Ch. et Ph.*, 3 Ser. iv. 77.)

BISULPHURETTED HYPOSULPHURIC ACID. TETRATHIONIC ACID. S_4O_5 . This acid was obtained by Fordos and Gélis (*Ann. Ch. et Ph.*, Decr. 1842) by carefully decomposing its combination with baryta by sulphuric acid, so diluted as to avoid elevation of temperature. The diluted acid may be boiled without decomposition, but, as it becomes concentrated, it deposits sulphur, evolves sulphurous acid, and the liquid acquires the property of precipitating barytic solutions. This acid is not affected by dilute hydrochloric or sulphuric acids, but nitric acid throws down sulphur. It does not precipitate the salts of iron, zinc, or copper; it gives a white precipitate with protochloride of tin and bichloride of mercury; a yellowish one, becoming black by excess of acid, with protonitrate of mercury; and with nitrate of silver, the precipitate, at first white, becomes speedily yellow and then black. (See *Bisulphuretted Hyposulphite of Soda*. See also in reference to the analytic separation of these acids a paper by Fordos and Gélis, *Ann. Ch. et Ph.*, Sept. 1843.) The elements of the bisulphuretted hyposulphuric acid may be represented as those of the sulphurous and hyposulphurous acid: thus

Sulphur	4	...	64	...	61·54	} = {	Sulphurous acid	1	...	32
Oxygen	5	...	40	...	38·46		Hyposulphurous acid	1½	...	72
<hr/>								<hr/>	<hr/>	<hr/>
Bisulphuretted hy- posulphuric acid....	1		104		100·00			1		104

SULPHUR AND CHLORINE. CHLORIDE OF SULPHUR. SCl . This compound was first described by Dr. Thomson, in 1804 (NICHOLSON'S *Journal*, vol. viii.); and afterwards more fully examined by Berthollet junior. (*Mém. d'Arcueil*, t. i.) The chlorides of sulphur have also been examined by Rose (*Poggend. Ann.*, xxi. 431), and by Dumas (*Ann. Ch. et Phys.*, XLIX. 205). When sulphur is heated in excess of dry chlorine, it absorbs rather more than twice its weight of that gas. Ten grains of sulphur absorb 30 cubic inches of chlorine, and produce a liquid of a greenish-yellow, by transmitted light, but orange red by reflected light. (DAVY. *Elements*, p. 280.) The combination also takes place at common temperatures, and may be effected by passing excess of dry chlorine through a tube containing powdered sulphur. It requires rectification to free it from dichloride, which should be performed between 140° and

160°. Chloride of sulphur exhales suffocating and irritating fumes when exposed to the air. Its specific gravity is 1.60. It boils at 146°, yielding vapor of the density of 3.70. It does not affect dry vegetable blues; but when water is present, it instantly reddens them, sulphur is deposited, and hydrochloric and hyposulphurous acids are formed, the latter being soon decomposed: $2 \text{ SCl}_2 + 2 \text{ H}_2\text{O} = 2 \text{ HCl} + \text{S}_2\text{O}_2$. It dissolves sulphur and phosphorus: it decomposes alcohol and ether: it is decomposed by mercury, heat being evolved, sulphur deposited, and chloride of mercury formed. A fragment of potassium dropped into it presently burns and explodes. It absorbs phosgene gas. According to Davy, although this compound readily dissolves sulphur, it is incapable of absorbing chlorine. From the analysis of Dumas it consists of

					Dumas.
Sulphur	1	16	30.7	31.4	
Chlorine	1	36	69.3	68.6	
Chloride of sulphur	1	52	100.0	100.0	

DICHLORIDE OF SULPHUR. BISULPHURET OF CHLORINE. SUBCHLORIDE OF SULPHUR. S_2Cl_2 . When the preceding liquid is saturated with sulphur, it deposits a portion, often in crystals, but retains, according to Bucholz, one additional proportional of sulphur, forming a yellow-brown liquid of the specific gravity of 1.686. It boils at 282°. The density of its vapor is 4.70. It is possessed of the general properties of the preceding. Tetrahedral crystals of sulphur may be obtained from this liquid, the deposition of which is much influenced by light. According to Rose (*Poggendorff's Ann.*, xxi.,) this is the only chloride of sulphur, and the preceding compound is a solution of chlorine in this dichloride. When dropped into water it gradually yields hydrochloric acid, sulphur, and hyposulphurous acid, the latter resolving itself into sulphurous acid and sulphur: $2 \text{ S}_2\text{Cl}_2 + 2 \text{ H}_2\text{O} = 2 \text{ HCl} + \text{SO}_2 + 3 \text{ S}$. Ether first dissolves and then gradually decomposes it, with slight elevation of temperature. It consists of

					Rose.	Bucholz.
Sulphur.....	2	32	47.0	47.06	47.4	
Chlorine	1	36	53.0	52.94	52.6	
Dichloride of sulphur	1	68	100.0	100.00	100.0	

When dichloride of sulphur is surrounded by a cooling mixture, it absorbs the vapor of anhydrous sulphuric acid, and produces a yellow liquid which is permanent at temperatures below 32°, but at a few degrees above 32° it evolves sulphurous acid. When this liquid is heated up to 50° sulphurous acid is rapidly evolved: between 86° and 104° chloride of sulphur passes over, and at 293° an oil-like liquid, which when freed by rectification from chloride of sulphur, is a *pentasulphate of terchloride of sulphur*: $= \text{SCl}_3, 5 \text{ SO}_3$. In its formation 3 atoms of dichloride of sulphur and 15 of anhydrous sulphuric acid, are resolved into 1 atom of this pentasulphate and 15 of sulphurous acid: $3 \text{ S}_2\text{Cl}_2 + 15 \text{ SO}_3 = \text{SCl}_3, 5 \text{ SO}_3 + 15 \text{ SO}_2$. Its composition therefore is

					H. Rose.
Sulphur.....	6	96	29.3	30.35	
Oxygen	15	120	37.0	38.15	
Chlorine	3	108	33.7	31.50	
Pentasulphate of terchloride } of sulphur	1	324	100.0	100.00	

AMMONIO-CHLORIDE OF SULPHUR. Two compounds of ammonia and chloride of sulphur have been described by Soubeiran. (*Ann. Ch. et Ph.*, LXvii. 71.) The one $= 2 \text{NH}_3 + \text{SCl}$; the other $\text{NH}_3 + \text{SCl}$: they are yellow, and brown compounds, crystallisable from their etherial solutions.

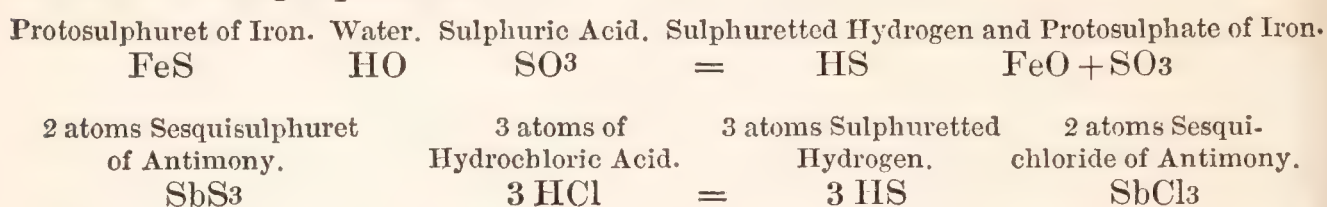
SULPHUR AND IODINE. IODIDE OF SULPHUR. SI. Sulphur and iodine readily unite by a gentle heat, and form a black crystalline compound. (GAY LUSSAC, *Ann. Ch.*, xci.) It is decomposed by a degree of heat a little exceeding that required for its formation, and, when boiled in water, the iodine goes off with the steam, and sulphur remains. It is probably a compound of one proportional of each of its components.

SULPHUR AND BROMINE. BROMIDE OF SULPHUR. SBr. When bromine is digested with sulphur, no heat is evolved, and a red liquid compound results, which emits fumes when exposed to air, and has little action upon dry litmus paper, but powerfully reddens it when moist. Under these circumstances, 1 atom of bromine dissolves 2 of sulphur. It dissolves both bromine and sulphur. It is slowly acted on by cold water, but at 212° the action is violent, sulphuretted hydrogen is evolved, and hydrobromic and sulphuric acids are formed. Chlorine decomposes the bromide of sulphur, and chloride of sulphur is formed, with the evolution of bromine. The composition of this bromide has not been accurately determined.

SULPHUR AND FLUORINE. SF. Davy obtained a fuming liquid, (*Fluoride of Sulphur* ?) by distilling a mixture of sulphur and fluoride of lead.

SULPHUR AND HYDROGEN. SULPHURETTED HYDROGEN GAS. HYDROTHIONIC ACID. HYDROSULPHURIC ACID. SULFHYDRIC ACID. HS. This compound was discovered by Scheele in 1777. When sulphur is heated or sublimed in hydrogen gas, or when the gas is passed through melted sulphur, a small portion of sulphuretted hydrogen is slowly formed, but the action is very imperfect. The gas is readily obtained when sulphur is presented to *nascent* hydrogen, which is the case when protosulphuret of iron is acted upon by dilute sulphuric acid, or when one part of bruised sulphuret of antimony is heated with four of hydrochloric acid; or one part of pulverized sulphur and two of iron filings may be made into a thin paste with water, and heated in a flask till the mixture blackens, after which, the addition of sulphuric acid diluted with four times its bulk of water, causes an abundant evolution of sulphuretted hydrogen. (GAY LUSSAC, *Ann. Ch. et Ph.*, vii. 314.) A mixture of equal parts of tallow and sulphur heated in a glass flask yields pure sulphuretted hydrogen. (REINSCH.) In the case of the evolution of sulphuretted hydrogen by the action of sulphuric acid and water upon the protosulphuret of iron, water is decomposed, its hydrogen combines with the sulphur of the sulphuret to form sulphuretted hydrogen, and its oxygen converts the iron into protoxide, which, combining with the sulphuric acid, forms protosulphate of iron: the gas is, however, apt to contain free hydrogen. When sesquisulphuret of antimony and hydrochloric acid are employed, sesquichloride of antimony is formed, and the hydrogen of the acid unites

to the sulphur of the sulphuret to form sulphuretted hydrogen: the gas in this case is slowly evolved, but it is pure. These reactions are expressed in the following equations:



Dumas recommends sulphuret of calcium, or the double sulphuret of sodium and iron obtained by fusing powdered pyrites with half its weight of dry carbonate of soda at a red heat, as sources of sulphuretted hydrogen when its rapid evolution is required; these sulphurets are to be acted on by hydrochloric acid.

Sulphuretted hydrogen is gaseous at common temperatures and pressures. Under a pressure of about 17 atmospheres at 50°, it assumes the liquid form: it is then limpid, and apparently possessed of a refractive power exceeding that of water; its specific gravity is about 0.9. When a tube containing it was opened under water, it instantly and violently rushed forth under the form of gas. (FARADAY, *Phil. Trans.*, 1823, p. 92.) When cooled to 122° below 0° it solidifies, and is then a white crystalline translucent substance, heavier than the liquid. At this temperature the pressure of its vapor is less than one atmosphere, so that the liquid allowed to evaporate in the air would not solidify, as is the case with carbonic acid. (FARADAY, *Phil. Trans.*, 1845, 164; where see also a table of the tension of its vapor at temperatures between -100° and +52°.)

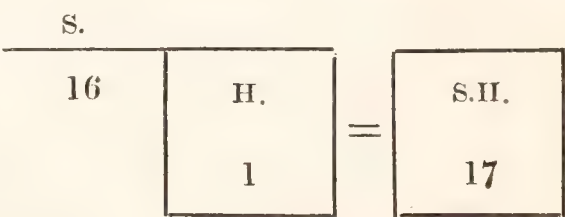
Sulphuretted hydrogen gas may be collected over warm water: by agitation cold water absorbs nearly thrice its bulk. It has a peculiarly nauseous fetid odor, resembling that of rotten eggs, and so diffusible that a single cubic inch escaping into the atmosphere of a large room, is soon every where perceptible by its smell. 100 cubic inches weigh 36.5366 grains. Its specific gravity compared with air is as 1.1786 to 1: and compared with hydrogen, as 17 to 1. According to Thomson its specific gravity is 1.1805; and 100 cubic inches, reduced to the temperature of 32°, weigh 38.6196 grains. Dumas gives its specific gravity as = 1.1912. It is inflammable, and during its slow combustion, sulphur is deposited, and water and sulphurous acid formed. It extinguishes the flame of a taper. When respired, it proves fatal; and it is very deleterious, even though largely diluted with atmospheric air. According to Dupuytren and Thenard, a small bird dies immediately in air containing only one 1500th of sulphuretted hydrogen; one 800th kills a middle-sized dog; and a horse is killed by an atmosphere containing one 150th. Nausea, vertigo, headache, and a peculiar faintness, are common consequences when an atmosphere even slightly contaminated by sulphuretted hydrogen is breathed for any length of time. When its escape in the laboratory cannot be prevented, its effects may be counteracted by the diffusion of a little chlorine, or by sprinkling the room with an aqueous solution of chlorine. It exists in some mineral waters, and is found in foul sewers and in putrid eggs.

The aqueous solution of sulphuretted hydrogen is transparent and colorless when recently prepared, but gradually becomes opalescent, and

if exposed to air deposits sulphur, and the greater part of the gas escapes. The whole of the gas is evolved by heat. It is an exceedingly delicate test of the presence of most of the metals, with which it forms colored precipitates. One measure of sulphuretted hydrogen mixed with 20000 measures of hydrogen, carburetted hydrogen, or atmospheric air, produces a sensible discoloration of white lead or of oxide of bismuth, mixed with water, and spread upon a piece of card. In this way we may ascertain the presence, in coal-gas, of extremely small quantities of sulphuretted hydrogen; and may even form an estimate of its proportion, when too minute to be otherwise measured, by comparing the shade of color with a series prepared for the purpose, by exposing slips of card covered with white lead and water to mixtures of sulphuretted hydrogen and common air, in known proportions. (HENRY, *Elements of Chemistry*.)

Sulphuretted hydrogen slightly reddens infusion of litmus, and moist litmus paper; it is generally classed among the hydracids, and does not, therefore, unite directly with the basic oxides, a metallic sulphuret and water being the usual result of their mutual reaction: (HS,MO=MS,HO,) it combines with certain sulphurets (basic sulphurets), and forms a class of *sulphur salts*; compounds, according to Graham, strictly analogous to the hydrated oxides, if we substitute sulphur for oxygen.

When hydrogen becomes sulphuretted hydrogen, its *volume* is unchanged: and when one volume of sulphuretted hydrogen is detonated with half a volume of oxygen, water is formed and sulphur precipitated; the whole of the mixed gases being condensed: but when a volume of sulphuretted hydrogen and a volume and a half of oxygen are inflamed in a detonating tube, one volume of sulphurous acid is produced, and water is formed. Thus the sulphur is transferred to one volume of the oxygen, and the hydrogen to the half volume. Sulphuretted hydrogen may also be decomposed by the Voltaic flame, in the apparatus shown in fig. 253, or by a succession of electric sparks: in either case its volume remains unchanged, but the sulphur is thrown down. This gas, therefore, consists of



				Berzelius.	Vols.	Sp. Gr.	100 C. I.
Sulphur	1	16	94.1	94.176	0.16	1.109	34.3
Hydrogen	1	1	5.9	5.824	1.00	0.069	2.1
Sulphuretted hydrogen	1	17	100.0	100.000	1.00	1.178	36.4

Spongy platinum does not effect the combustion of a mixture of sulphuretted hydrogen and oxygen unless free hydrogen be also present.

Chlorine, iodine, and bromine, instantly decompose sulphuretted hydrogen; when they are not in excess sulphur is deposited, and hydrochloric, hydriodic, and hydrobromic acids are formed. Nitric acid poured into the gas occasions a deposition of sulphur, and nitrous acid and water are formed, with considerable elevation of temperature, and occasionally flame. The aqueous solution of the gas is also decomposed by these reagents. Hence the method of preparing hydriodic and hydrobromic acids by passing sulphuretted hydrogen through water in which iodine or bromine is diffused, as already noticed. When sulphuretted hydrogen is

mixed with its volume of nitric oxide over mercury, a diminution of bulk ensues, in consequence of the production of water; sulphur is deposited, and nitrous oxide remains in the vessel. ($\text{HS} + \text{NO}_2 = \text{HO} + \text{S} + \text{NO}$.) When *two* volumes of sulphuretted hydrogen are mixed in an exhausted balloon with *one* of sulphurous acid, they mutually decompose each other, occasioning the production of water, and the deposition of sulphur; ($2\text{HS} + \text{SO}_2 = 2\text{HO} + 3\text{S}$.) If the gases be perfectly dry, the action is slow. According to Thomson, the deposited matter is not sulphur, but a compound of sulphur, oxygen, and hydrogen, which he calls *hydrosulphurous acid*. (*Ann. of Phil.*, xii. 441.) Sulphuric acid also decomposes sulphuretted hydrogen; the results are water, sulphurous acid, and sulphur, ($\text{HS} + \text{SO}_3 = \text{HO} + \text{SO}_2 + \text{S}$): but if the acid be diluted with 4 or 5 parts of water, it has no action, and if in that case it is rendered turbid by sulphuretted hydrogen, the presence of sulphurous or arsenious acids may be suspected.

When potassium or sodium are heated in sulphuretted hydrogen, sulphur-salts of those metals are formed with vivid combustion, and pure hydrogen is liberated: ($\text{K} + 2\text{HS} = \text{KS}, \text{HS} + \text{H}$.) When tin or lead are fused in the gas, they also decompose it, and absorb the sulphur, leaving a volume of hydrogen equal to that of the original gas. Passed over metallic oxides, water and metallic sulphurets are, as above stated, the results: the different oxides effect this decomposition at very different temperatures.

SULPHURETTED HYDROGEN AND AMMONIA. HYDROSULPHURET OF AMMONIA. HYDROSULPHATE OF AMMONIA. SULPHURET OF AMMONIUM. BOYLE'S FUMING LIQUOR. BEGUIN'S SULPHURETTED SPIRIT. NH_3, HS , or NH_4, S . When ammonia and sulphuretted hydrogen gas are mixed, fumes at first appear, and a crystallized compound results. If this be obtained by the condensation of 1 volume of sulphuretted hydrogen and 2 of ammonia, it may be considered as consisting of 1 proportional of each of its components. The only way of combining the gas in these proportions is to suffer them, previously dried, to pass by separate tubes to the bottom of a flask or bottle immersed in ice; the access of air should be prevented, and the escape of any uncondensed gas provided for by a safety-tube; the crystals thus produced are at first colorless, and when exposed to air lose half their ammonia. This protosulphuret of ammonium is also formed when sal-ammoniac and sulphuret of calcium are distilled together. ($\text{CaS}, \text{NH}_4\text{Cl} = \text{CaCl}, \text{NH}_4\text{S}$.) Its aqueous solution may be obtained by dividing aqueous ammonia into 2 equal parts, saturating one with sulphhydrogen, and then adding to it the other: it forms a colorless sulphuretted liquid, which decomposes in the air. ($\text{NH}_4\text{S}, \text{HS} + \text{NH}_3 = 2\text{NH}_4\text{S}$.) It consists of

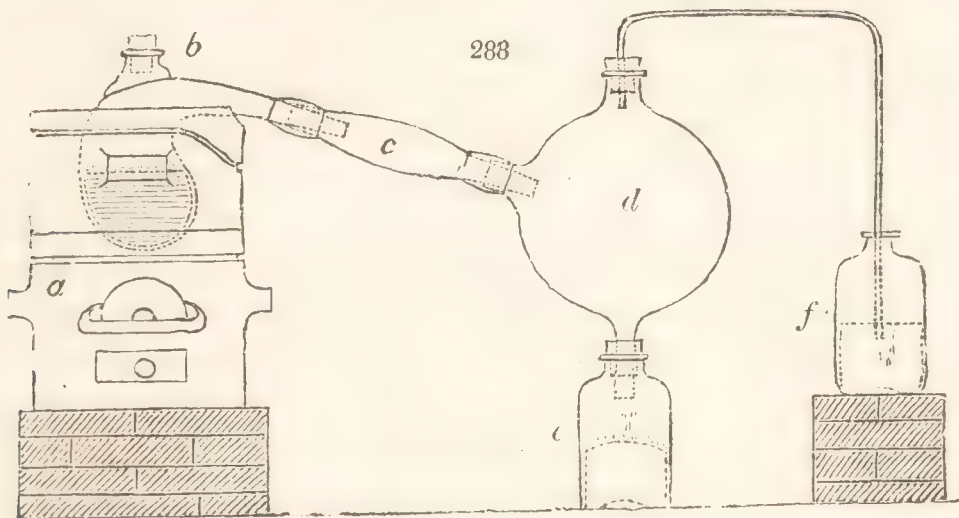
Volumes.									
Ammonia	1	17	50	2	} = {	Ammonium.....	1	18	53.9
Sulphuretted hydrogen	1	17	50	1		Sulphur	1	16	46.1
<hr/>									
Hydrosulphuret of am- monia	}	1	34	100	}	Sulphuret of ammonium....	1	34	100.0

BIHYDROSULPHURET OF AMMONIA. $\text{NH}_3, 2\text{HS}$. HYDROSULPHURET OF AMMONIUM. $\text{NH}_4\text{S}, \text{HS}$. When equal volumes of ammonia and sulphuretted hydrogen are brought together in a cooled vessel, volatile

colorless crystals are deposited, which become yellow by exposure. The aqueous solution of this compound is formed by saturating solution of ammonia with sulphuretted hydrogen. This compound may be regarded as a sulphur-salt of ammonium; its components are

Ammonia	1	17	33·33	} = {	Sulphuret of ammonium	1	34	66·67
Sulphuretted hydrogen	2	34	66·67		Sulphuretted hydrogen	1	17	33·33
<hr/>								
Bihydrosulphuret of ammonia.....	}	1	51	100·00	}	Hydrosulphuret of ammonium.....		
						1	51	100·00

PERSULPHURET OF AMMONIUM. *Boyle's fuming liquor of Sulphur. Beguin's Spiritus Sulphuratus.* A compound of sulphuretted hydrogen and ammonia, with excess of sulphur, is obtained by distilling a mixture of about 4 parts of slaked quicklime, 2 of hydrochlorate of ammonia, and 1 of sulphur. The following is the disposition of the apparatus for this experiment: (see fig. 288) *a* is a small furnace; *b*, a tubulated earthen retort containing the above materials; *c*, an adapting tube; *d*, a glass balloon for condensing the vapor; *e*, a receiver; *f*, a bottle of water, into



which the glass tube, issuing from the upper part of the balloon *d*, is made to dip about half an inch. The product in the receiver *e*, may be mixed with the water in *f*, and the whole used for washing out the balloon *d*. In its concentrated state, this compound exhales white fumes, and was formerly called *Boyle's fuming liquor*. It is a deep yellow liquid, smelling like a mixture of sulphuretted hydrogen and ammonia. It dissolves sulphur. According to Gay Lussac (*Ann. Ch. et Ph.*, XL. 302), no ammonia is decomposed in the above operation, but the sulphuretted hydrogen is formed by the union of sulphur with the hydrogen of the hydrochloric acid: the residue in the retort, consisting of sulphate of lime and chloride and sulphuret of calcium, is formed by the union of sulphur with part of the oxygen of the lime to produce sulphate of lime, the evolved calcium being divided between the chlorine and sulphur.

When sulphur is digested in either of the hydrosulphurets of ammonia, yellow solutions are obtained, probably containing several definite sulphurets; two crystalline compounds of this kind have been described by Fritzsche, the one containing 5, and the other 7 atoms of sulphur, and 1 of ammonium, namely, NH_4S_5 , and NH_4S_7 . All the yellow hydrosulphurets yield precipitates of sulphur on the addition of acids. They are used as tests of the presence of several of the metals, and have been employed in medicine, principally in diabetes, and as a sudorific in gout.

PERSULPHURET OF HYDROGEN. SUPERSULPHURETTED HYDROGEN. HS₂. This is a yellow liquid, first described by Berthollet, (*Ann. de Chim.*, XXV.,) formed by dropping a strong solution of persulphuret of potassium into dilute hydrochloric acid (see *Sulphurets of Potassium*). If the acid be dropped into the sulphuretted solution, sulphuretted hydrogen escapes, and sulphur is precipitated; but proceeding as above directed, the greater part of the sulphur remains united to the hydrogen, and a peculiar yellow liquid is the result. The success of the experiment depends much upon the state of concentration of the alkaline solution, which should neither be too strong nor too dilute, and should be slightly warm, and stirred during the mixture.

Persulphuret of hydrogen may also be obtained by boiling 1 part of slaked lime and 2 of flowers of sulphur, in 15 parts of water, for about half an hour; when cold, the supernatant brown liquor (containing hydrosulphuret of lime, with excess of sulphur) is to be poured off, and gradually added to hydrochloric acid, either of its usual strength, or diluted with its bulk of water, taking care to have excess of acid, and to stir the mixture after each addition. Under these circumstances some sulphur is precipitated, and the sulphuretted hydrogen is not evolved, but unites to an additional proportion of sulphur to form the persulphuret, which gradually subsides in the form of a yellow viscid fluid, which may be kept for some days in the acid liquor, or in dilute hydrochloric acid. Its specific gravity is about 1.7. Its odor is pungent and irritating; its taste sweetish and bitter. It is often involved in a coating of sulphur, from which it may be squeezed out by gentle pressure with a glass rod. In water it is slowly resolved into sulphur and sulphuretted hydrogen, and more rapidly by alkaline solutions. At 212° it is rapidly decomposed. Oxide of gold or silver is immediately reduced by it with slight explosion and incandescence. Other substances, such as the metals, silica, and the alkaline earths, decompose it, without themselves suffering change. Thenard (*Ann. Ch. et Ph.*, XLVIII. 79,) suggests an analogy between it and peroxide of hydrogen, in consequence of its possessing slight bleaching power, and producing a white spot upon the skin. Its composition has not been accurately determined, but from the mode of its formation it is by some regarded as a pentasulphuret of hydrogen: HS₅. Thus, in its formation, by adding solution of pentasulphuret of potassium to hydrochloric acid, the following formula may represent the change: $KS_5 + HCl = KCl + HS_5$. L. Gmelin observes, in reference to the solutions from which this compound is precipitated, that they may either contain it in combination with an alkali, or that they may be regarded as holding a pentasulphuret: thus, when pentasulphuret of potassium is dissolved in water, we have $(KS_5 + HO = KO, HS_5)$; or when sulphur is digested in a solution of a protosulphuret so that 4 atoms of it are dissolved $(KS + 4S = KS_5; \text{ or } KO, HS + 4S = KO, HS_5)$. When sulphur is boiled with an aqueous solution of a fixed alkali, or with lime, a hypsulphite is at the same time formed: thus, $3CaO + 12S = 2CaS_5 + CaO, S_2O_2$: or $3CaO + 12S + 2HO = 2CaO, HS_5 + CaO, S_2O_2$.

SULPHUR AND NITROGEN. TERSULPHURET OF NITROGEN. NS₃. By the action of chloride of sulphur on dry ammonia, an *ammonio-chloride of sulphur* is formed $= 2NH_3, SCl$, which is resolved by cold water into

hydrochlorate, and hyposulphite of ammonia, and sulphuret of nitrogen: the latter is a greenish-yellow powder, which is to beedulcorated with cold water, then washed with alcohol, pressed in filtering paper, and rapidly dried in vacuo over sulphuric acid. It may be obtained crystallised from its solution in ether: it is inodorous and nearly tasteless. By heat it is resolved into nitrogen and sulphur. By water it is gradually changed into hyposulphurous acid and ammonia. ($2 \text{NS}_3 + 6 \text{HO} = 2 \text{NH}_3 + 3 \text{S}_2\text{O}_2$.) (SOUBEIRAN, *Ann. Ch. et Ph.*, LXvii. 71.) “When aqua ammoniæ acts on chloride of sulphur, a variety of products are formed; among which is one, a white crystallisable solid soluble in alcohol, which appears to consist chiefly of sulphur and nitrogen: its nature is not yet ascertained, but it is distinguished by the property of dissolving in an alcoholic solution of potassa, with a deep purple color, which soon disappears, while ammonia is given off and crystals of hyposulphite of potassa are deposited.” (GREGORY.) The composition of the sulphuret described by Soubeiran, appears to be

Sulphur	3	48	22·58
Nitrogen	1	14	77·42
<hr/>					
Tersulphuret of nitrogen	1		62		100·00

CHLOROSULPHURET OF NITROGEN. NS_4Cl , or NS_3, SCl . This compound is obtained mixed with sal-ammoniac by exposing the combination of 1 atom of ammonia and 1 of chloride of sulphur for some hours to a heat of 212° . $4 [\text{NH}_3, \text{SCl}] = 3 [\text{NH}_4, \text{Cl}] + \text{NS}_4\text{Cl}$. It has a peculiar odor, and at higher temperature is resolved into sal-ammoniac, nitrogen, chloride of sulphur, and sulphur. $\text{NS}_4\text{Cl} = \text{N} + \text{S}_2\text{Cl} + 2 \text{S}$. (SOUBEIRAN, *Ann. Ch. et Ph.*, LXvii.)

§ IX. PHOSPHORUS. P. 32.

Phosphorus, so termed from its property of shining in the dark, (from *φωσ*, *light*, and *φερειν*, *to bear*,) occurs in the three kingdoms of nature, but most abundantly as a component of the bones and in the urine of the higher orders of animals: it is almost always present as phosphoric acid, combined with various bases. It was discovered in 1669 by Brandt, a merchant of Hamburg; he obtained it whilst attempting to extract from urine a liquid capable of converting silver into gold. (HOMBERG, *Mém. Par.*, x. 84.) Kunckel, a German chemist, aware of the source whence it was obtained, imparted the secret to Kraft of Dresden, who repaired to Hamburg to learn the details of the process, for which he paid Brandt two hundred dollars; but in the mean time Kunckel (*Laboratorium Chemicum*, Hamb., 1716,) prepared and described it, and was therefore considered as one of its discoverers. In 1680 an account of it was published in the *Phil. Trans.*, and it became known under the name of *English Phosphorus*, in consequence of the large quantities of it prepared in London, under the direction of the celebrated Boyle, by his assistant, Godfrey Hankwitz*. In 1737 a process for its preparation was sold by

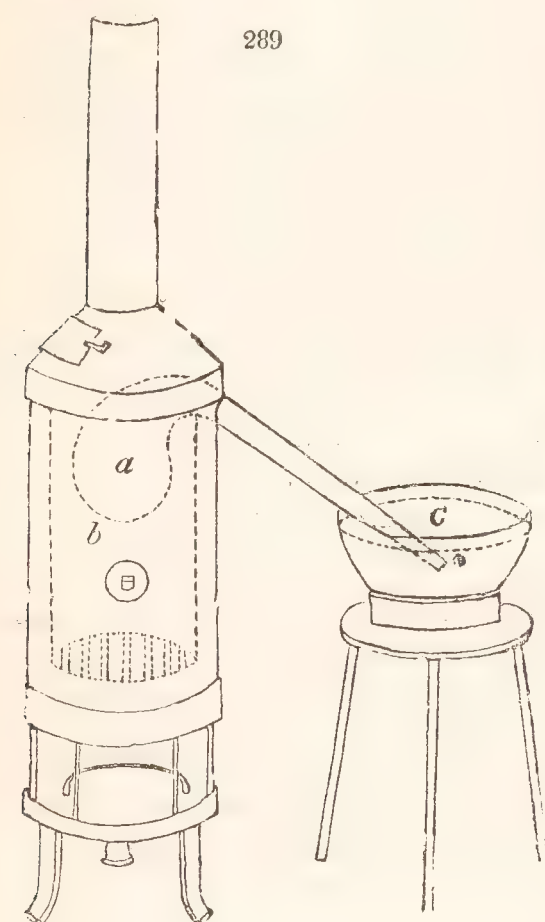
* The founder of the Chemical Establishment, long known as “Godfrey’s,” in Southampton Street, Covent Garden. I have a print of this Chemist, by Vertue, which, it is said, he presented to his

customers on taking leave of them to sell phosphorus abroad: he is surrounded with the apparatus used in preparing it. Boyle described the process in a little work, entitled *Aërial Noctiluca*.

a stranger, to the French government, an account of which was published by Hellot. (*Mém. de l'Acad.*, 1737.) It was tedious and disgusting: from five (muids) hogsheads of urine 38 pounds of residue were obtained by evaporation, and this, by four distillations, yielded at most 4 ounces of phosphorus. The process was improved by Margraff, Gahn, and Scheele, and afterwards by Fourcroy and Vauquelin.

Since the introduction of *Lucifer matches* the consumption of phosphorus has enormously increased, and it is largely prepared in London, Paris, and various parts of Germany. "It is computed that in Paris 200,000lbs. of phosphorus are obtained annually." (KANE.)

Phosphorus may be obtained on the small scale, by distilling phosphoric acid, previously fused with one-fourth its weight of powdered charcoal, in the open fire. This mixture is pulverized and put into a coated green-glass or stone-ware retort *a* (fig. 289), placed in the furnace *b*; the tube of the retort should be immersed about half an inch into the basin of water *c*. A quantity of gas escapes, some of which is spontaneously inflammable, and when the retort has obtained a bright red heat, a substance looking like wax, of a reddish color, begins to pass over. This, which is impure phosphorus, may be ren-



dered pure by melting it under warm water, and squeezing it through a piece of fine shamoy leather; but great care must be taken that none adheres to the nails or fingers, as it would inflame on taking them out of the water, and produce a painful and troublesome burn. In performing this distillation, a high temperature is required, so that the furnace should be sufficiently capacious to hold a body of coke or charcoal piled up above the retort, which, especially if of earthenware, (which becomes permeable to the vapor of phosphorus, at a red heat,) must be coated with a mixture of slaked lime and solution of borax; this mixture may be laid on with a brush, in two or three successive coats, and forms an excellent *vitriifiable lute*.

Phosphorus may also be obtained by adding solution of nitrate of lead or nitrate of mercury to urine, collecting, washing, and drying the precipitate, and distilling it, as above, with a fourth its weight of powdered charcoal. These precipitates are impure phosphates of lead and mercury; the latter is the easiest of decomposition.

Upon the large scale, phosphorus is most economically procured from the superphosphate of lime obtained by acting upon powdered *bone earth* by dilute sulphuric acid. The following is the mode of proceeding:

On twenty pounds of calcined bone, finely powdered, pour twenty quarts of water, and eight pounds of sulphuric acid, previously diluted with an equal weight of water. Let these materials be stirred together,

and simmered for about six hours. Let the whole be then put into a conical bag of linen to separate the clear liquor, and wash the residuum till the water ceases to taste acid. Evaporate the strained liquor, and when reduced to about half its bulk, let it cool. A white sediment will form, which must be allowed to subside; the clear solution must be decanted, and boiled to dryness in a glass vessel. A white mass will remain, which may be fused in a platinum crucible, and poured out into a clean copper dish. A transparent substance is thus obtained, consisting of phosphoric acid, with phosphate, and a little sulphate of lime, commonly known under the name of *glass of phosphorus*. (See, in reference to this decomposition, *Phosphate of Lime*.) It yields phosphorus when distilled at a bright red heat with charcoal, in the way above described; but when any quantity of phosphorus is to be collected, the retort should be very well and carefully luted, and should have a wide neck terminating in a copper tube, so bent as to dip perpendicularly into a bottle of water, otherwise it will be apt to become plugged up by congealed phosphorus. The phosphorus is generally sufficiently purified by fusing it in hot water, and when cold, cutting it into small pieces, which are put with water into a slightly conical glass tube, and fused by immersion in hot water: on cooling, the phosphorus is withdrawn in the form of a stick. (See also an apparatus for giving the stick form to phosphorus described in *Pharm. Journ.*, iv. 129.) If the phosphorus is much discolored, it may be cleansed by fusing it first in warm caustic ammonia, and then in alcohol.

Wöhler recommends instead of the preceding process, to calcine 2 parts of ivory-black (which is a mixture of phosphate of lime and charcoal), with 1 of fine quartz sand, and a little ordinary charcoal, in cylinders of fire-clay, at a very high temperature. Each cylinder has a bent copper tube adapted to it, one branch of which descends into a vessel containing water. The efficiency of this process depends upon the silica acting as an acid and combining with the lime of the phosphate at a high temperature, while the liberated phosphoric acid is decomposed by the carbon. (GRAHAM.)

When pure, phosphorus is tasteless, because insoluble; when in solution it has a sharp nauseous taste: it is colorless, or of a very pale buff color, semitransparent, and flexible at common temperatures, but at 32° , crystalline and brittle. It is also rendered brittle, at higher temperatures, by the presence of less than a two-hundredth part of sulphur. Exposed to air it exhales luminous fumes, having a peculiar odor, distantly resembling that of garlic. Its specific gravity is 1.9 to 2. Its specific heat, as ascertained, apparently with accuracy, by Regnault, is 0.1887, but Dulong and Petit give 0.385 as the average result of their experiments. (*Ann. Ch. et Ph.*, Lxxiii. 55.) It is a non-conductor of electricity both in its solid and fluid state. (FARADAY.) According to Knox, fused phosphorus transmits the electricity of 60 pair of zinc plates. (*Phil. Mag.*, xvi. 188.) It is insoluble in water, but it dissolves sparingly in absolute alcohol, in ether, oils, naphtha (and most of the liquid hydrocarbons) and abundantly in sulphuret of carbon; the chlorides of sulphur and of phosphorus also dissolve it. By slowly cooling some of its hot saturated solutions, it may be obtained in rhombic dodecahedrons. When fused with about half its weight of sulphur and gradually cooled, part of the phosphorus separates in crystals. (MITSCHER-

LICH, *Ann. Ch. et Ph.*, xxiv. 270.) It melts, when air is excluded, at about 110° , undergoing a remarkable dilatation of 0.031 of its volume: it is very brittle at a temperature of 94° . (J. DAVY, *Ed. Phil. Journ.*, vi. 130.) If suddenly cooled to 32° , after having been heated to 140° , it sometimes becomes black (THENARD); but if slowly cooled, always remains colorless. "When fused and left undisturbed, it sometimes remains liquid for hours at the usual temperature, particularly when covered by an alkaline liquid." (GRAHAM.) Under these circumstances its temperature suddenly rises in the act of solidification to about 100° . (DUMAS.) At 550° (DALTON,) 572° (GREGORY,) it boils and evaporates in the form of colorless vapor, the density of which, according to Dumas, is 4.355. But phosphorus evaporates, especially if in contact with moisture, at a much lower temperature. The volatility of phosphorus in conjunction with aqueous vapor is shown by boiling a flask of water containing a piece of phosphorus, over a lamp; the vapor, as it issues from the flask, is luminous in a dark room. It has been used in medicine in very small doses: it acts as a powerful and diffusible stimulant, exciting the nervous, vascular, and secreting organs; in larger doses it causes vomiting, purging, and inflammation of the stomach and bowels: its activity depends, according to Orfila, on its absorbing oxygen, and becoming converted into an acid, which acts like other mineral acids, as a corrosive. Instances are on record in which a grain and a half, and 3 grains, have proved fatal (CHRISTISON); but on the other hand it is said, that from 6 to 12 grains have been swallowed without hurtful effects. "I once administered 16 grains of apparently good phosphorus to a man without any injurious effect. The person here alluded to, was Chabert, some years ago renowned in London as the '*Fire King*.' I carefully weighed the above quantity, which was placed in a spoon, introduced into his mouth, and washed down by a tumblerful of water. He offered to take the dose daily. Within ten minutes after swallowing the phosphorus he left the room for a quarter of an hour." (PEREIRA, *Mat. Med.*) In all probability, during his absence from the room, he got rid of the phosphorus by vomiting.

The redistillation of phosphorus is sometimes resorted to for the purpose of purification, but the process is troublesome, and as far as arsenic is concerned ineffective, for that substance goes over along with the phosphorus. Dr. Henry gives the following directions for it: "The proper quantity of phosphorus should first be put into the retort, with a sufficient portion of water to cover it. The water must then be made hot enough to melt the phosphorus, which, on cooling, forms a mass, of the shape of the bottom of the retort. When cold, fill the retort with water, and invert it in water. Displace the water by hydrogen gas, forced from a bladder through a bent pipe; keep the finger on the open end of the retort neck; place it in a sand-bath; and immerse the mouth of it in water. Then apply heat very cautiously. A bladder should also be provided, furnished with a stop-cock and pipe, and filled with hydrogen. During the distillation, the gas in the retort is absorbed, and it is necessary to add more from the bladder, otherwise the water will rush into the retort, and occasion an explosion. By distillation in this mode, phosphorus is rendered much purer. In the neck of the retort a substance is condensed of a beautiful red or carmine color, which is a combination of

carbon and phosphorus, or a *phosphuret of carbon*." Thenard observes that phosphorus, however frequently distilled, cannot be freed entirely from carbon, a minute quantity of which does not impair its color or transparency.

Wittstock found in a scruple of commercial phosphorus, as much as 0.76 per cent. of arsenic: it was entirely soluble in sulphuret of carbon, but soon deposited a red sediment, consisting of sulphuret of arsenic and oxide of phosphorus. (*Poggend. Ann.*, xxxi. 126.) The arsenic is recognised by digestion in nitric acid, which acidifies it, and it may then be detected by sulphuretted hydrogen. Bismuth, lead, iron, copper, and especially antimony, have also been found in the phosphorus of commerce.

Retained for some time immersed in water, phosphorus decomposes it; oxide of phosphorus, and phosphorous and phosphoric acids are formed, and phosphuretted hydrogen is emitted. Phillips has observed that these changes are most rapid when light has free access. (*Ann. Phil.*, v.) The nature of the white crust which envelops phosphorus that has long been preserved under water, has, however, not been accurately ascertained. Rose regards it as merely an altered state of aggregation. According to Pelouze it is a *hydrate*. (*Ann. Ch. et Ph.*, L. 83.) A stick of phosphorus exposed by partial immersion to the joint action of air and water gradually runs down into the acids of phosphorus, which are found dissolved in the water. According to Berzelius, light, and especially violet light, has the peculiar effect of reddening phosphorus under whatever circumstances it is exposed to its influence; in nitrogen gas, the concentrated solar rays readily fuse it, but in hydrogen and in vacuo, they cause it to sublime in red scales.

There are several peculiar circumstances respecting the luminosity and inflammability of phosphorus. When exposed to the air at temperatures above the freezing-point, it shines in the dark with a pale blue light, which increases in intensity with the temperature. This arises from slow combustion, attended by the production of acid: it ceases in close vessels as soon as the greater part of the oxygen has been absorbed; and it is said not to take place when the air has been artificially dried: in this case the formation of phosphorous acid seems to be prevented. In pure oxygen, phosphorus is not luminous till heated to between 70° and 80° , above which it becomes very luminous, and soon inflames. Oxygen, and most other gases, in which phosphorus has been immersed, acquire its odor, and when mixed with air become slightly luminous. According to Dr. Henry, if a piece of phosphorus be introduced into a vessel of oxygen gas over mercury, at a temperature not exceeding 80° , no perceptible absorption will happen in twenty-four hours; but if, the temperature remaining the same, the pressure be diminished to one-eighth or one-tenth that of the atmosphere, the phosphorus will be surrounded with white vapors, will become luminous in the dark, and will absorb oxygen. Under ordinary pressures, a higher temperature is required for this effect; but if the density of the oxygen be reduced in the above proportion by mixing it with nitrogen, hydrogen, or carbonic acid, the phosphorus becomes luminous. Graham has shown that the slow combustion of phosphorus in air, is prevented by very small additions of certain gases and vapors. (*Quart. Journ.*, N.S., vol. vi. p. 83.) Thus at the temperature 66° it is entirely prevented by one volume of olefant

gas in 450 volumes of air, by one volume of ether vapor in 150 volumes of air, by one volume of naphtha vapor in 1820, and of oil of turpentine vapor in 4444 volumes of air. This influence is not confined to low temperatures, for a certain admixture of the above vapors will even prevent the oxidation of phosphorus at 200° ; but on allowing such gaseous mixtures to expand, by diminishing the pressure upon them, the phosphorus becomes luminous, and the proportion of foreign gas required to prevent oxidation or slow combustion must be much increased. "The only explanation," Mr. Graham observes, "of this phenomenon which can be offered, is that the gases which exert this influence have an attraction for oxygen, and there is reason to believe are themselves undergoing a slow oxidation at the same time. Now when two oxidable bodies are in contact, one of them often takes precedence in combining with oxygen to the entire exclusion of the other. Potassium is defended from oxidation in air by the same vapors, though to a less degree."

In the vacuum of the air-pump, phosphorus in small pieces, loosely enveloped in cotton, will generally inflame and burn for a time with a pale light: under the same circumstances it more readily kindles if sprinkled with powdered resin or sulphur; alone it does not inflame. When a stick of phosphorus is sprinkled with lamp-black, or powdered animal charcoal, it is also apt to inflame; and, what is curious, when very thin slices of phosphorus are placed upon flannel, wool, lint, fine feathers, or other downy and flocculent substances, they fuse and readily inflame upon the gentlest friction. It seems as if the slow combustion of the phosphorus produced heat enough to fuse it whilst lying upon a very bad conductor. If several pieces of phosphorus be placed upon each other, they are also apt to inflame. Berzelius remarks, that the water in which phosphorus has been kept in perfectly closed vessels, acquires a luminous property when agitated; this is not the case when air has access.

The actual temperature at which phosphorus inflames has been variously stated. According to Dr. Higgins, when perfectly dry, a temperature of 60° is sufficient. It easily takes fire by the heat of the hand and slight friction, or when rubbed upon a piece of coarse paper: it requires therefore to be handled and wiped with the utmost caution. Owing to the superficial formation of phosphorous and phosphoric acid, when it burns imperfectly at low temperatures, its further combustion is often prevented: thus, in rubbing a fragment of phosphorus between two pieces of brown paper, a momentary combustion often ensues, and it requires considerable friction to cause it again to inflame; for the same reason it is very difficult to light a piece of paper by the flame of phosphorus, for the paper becomes covered and protected by the acid. So also small pieces of phosphorus may be fused by the gradual application of heat, but will not inflame till the surface is disturbed by touching it with a wire.

When in brilliant combustion in the air, phosphorus throws off copious fumes of phosphoric acid, and its flame is intensely luminous (p. 127); but if it be heated in a confined portion of very rare air, it enters into less perfect combustion, and three compounds of phosphorus with oxygen are the result, each characterized by distinct properties. The first is a red solid, less fusible than phosphorus; the second a white substance, more volatile than phosphorus; the third, a white and more fixed body.

The red solid consists of a mixture of phosphorus and oxide of phosphorus. A somewhat similar mixture may be obtained by putting a piece of phosphorus into a small phial, and melting and stirring it about by a hot wire, so as to line the interior; a little of it taken out upon the end of a sulphur match presently inflames; and if the phial be kept well closed, it may be thus used for many months without deterioration, and forms a simple and convenient source of instantaneous light. (NICHOLSON'S *Journ.*, vi. 134.)

The different products of the combustion of phosphorus are well shown by heating a fragment of it placed near the centre of a thin glass tube of about a fourth of an inch diameter, and three or four feet long, and then gently driving a current of air through the tube; the fixed and volatile acids, and the red oxide, are in this way distinctly separated.

The equivalent of phosphorus formerly adopted, was 16 (15·7 BERZELIUS. TURNER. GREGORY.); but the number 31·44, adopted by Graham and by Gmelin, may more properly be said to represent its least combining quantity. I shall use the number 32 as sufficiently agreeing with the best analyses of its combinations, the peculiarities of the atomic constitution of which will be seen from the following table of its compounds with oxygen.

Oxide of phosphorus	P ₂ O
Hypophosphorous acid	PO
Phosphorous acid	PO ₃
Phosphoric acid.....	PO ₅

OXIDE OF PHOSPHORUS, P₂O, is formed by throwing a jet of oxygen gas into phosphorus fused under hot water; vivid combustion ensues, phosphoric acid is formed, and at the same time a red pulverulent oxide deposited, which is freed from water and unoxidized phosphorus by heating it in a retort; it is then again washed and dried in vacuo over sulphuric acid. It is insoluble in water, ether, alcohol, and oils; difficultly inflammable when heated in the air, but instantly burns upon contact of nitric acid.

According to Le Verrier, a definite oxide of phosphorus is obtained by exposing small fragments of phosphorus, covered by the liquid chloride of phosphorus, to the action of air: phosphorous and phosphoric acids are formed, and at the same time a yellowish substance, which he regards as a phosphate of the oxide of phosphorus, and which yields a yellow solution with water. At a temperature of about 176° this solution is decomposed, and a yellow flocculent substance subsides, which is a hydrated oxide of phosphorus, but which, when dried in vacuo over sulphuric acid, loses its combined water. In this state it is a yellow powder insoluble in water, alcohol, and ether. It resists a temperature of 570° without decomposition, but acquires a red color: it does not burn till heated somewhat beyond the boiling point of mercury. (PELOUZE, *Ann. Ch. et Ph.*, L. 83. LEVERRIER, *ibid.* LXV. 257.)

					Leverrier.	Pelouze.
Phosphorus	2	64	88·8	88·64	85·5	
Oxygen	1	8	11·2	11·36	14·5	
Oxide of phosphorus	1	72	100·0	100·00	100·0	

HYPOPHOSPHOROUS ACID. PO. was discovered by Dulong in 1816. (*Ann. Ch. et Ph.*, II. 141.) It is prepared as follows: Upon 1 part of
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phosphuret of barium pour 4 parts of water, and when the evolution of phosphuretted hydrogen gas has ceased, pour the whole upon a filter. To the filtered liquid add sulphuric acid as long as any precipitate forms: separate the precipitate, which is sulphate of baryta, and the clear liquor now contains the hypophosphorous acid in solution. When concentrated by evaporation, a sour viscid liquid is obtained, incapable of crystallization, and eagerly attractive of oxygen.

Rose obtained hypophosphorous acid by boiling hydrate of baryta with water and phosphorus, till all garlic odor ceased, filtering the liquid and decomposing it by excess of sulphuric acid; separating the precipitate, and digesting the clear fluid for a short time with excess of oxide of lead; then filtering the solution of *hypophosphite of lead* from the sulphate of lead, and decomposing it by a current of sulphuretted hydrogen. The acid, freed from the precipitated sulphuret of lead, was concentrated until of sufficient strength. (*Poggend. Journ.*, ix. and xii.) It is of the consistence of syrup, uncrystallizable, and very sour: it has not been obtained free from water: the elements of the anhydrous acid are

					H. Rose.	Dulong.			
Phosphorus.....	1	...	32	...	80	...	79.69	...	73.4
Oxygen	1	...	8	...	20	...	20.31	...	26.6
<hr/>									
Anhydrous hypophosphorous acid	1	40	100	100.00	100.0			

In a memoir on the acids of phosphorus, by Wurtz, (*Ann. Ch. et Ph.*, January, 1843,) this acid is regarded as containing hydrogen as an essential element; he represents it by the formula $\text{PH}_2\text{O}_3 (= \text{PO}, 2\text{HO})$; and in reference to this view of its constitution, the *hypophosphites* have the formula $\text{MO} + \text{PH}_2\text{O}_3$ (instead of $\text{MO}, \text{PO}, + 2\text{HO}.$) These views are opposed by H. Rose, (*Ann. Ch. et Ph.*, July, 1843); but his objections are replied to by Wurtz in a second memoir (*Ann. Ch. et Ph.*, February, 1846,) in which he adduces additional evidence in favor of his former hypothesis, founded upon a series of analyses of the hypophosphites.

When hydrated hypophosphorous acid is heated, it is decomposed with the evolution of phosphuretted hydrogen, and phosphoric acid is the residue: $2\text{PO}, + 3\text{HO} = \text{PH}_3 + \text{PO}_5$. It is a powerful deoxidizing agent. In combination with bases it forms *hypophosphites*; they are soluble in water, and many of them in alcohol; they are decomposed by a red heat: they are mostly deliquescent and uncrystallizable. (DULONG.)

HYPOPHOSPHITE OF AMMONIA. This salt is extremely soluble, deliquescent, difficultly crystallizable, and soluble in alcohol. When heated ammonia is evolved and hydrated hypophosphorous acid remains, which is decomposed when more highly heated. (H. ROSE, *Poggend.* xii., 85.) Wurtz obtains this salt by the action of hypophosphite of baryta on sulphate of ammonia: it crystallizes in irregular hexagonal tables permanent at 212° ; it fuses without loss of water at about 320° , and concretes into a crystalline mass on cooling: at about 464° it is decomposed with the evolution of phosphuretted hydrogen and a little water: its formula is $\text{NH}_3, \text{PO}, 3\text{HO} = \text{NH}_4\text{O}, \text{PH}_2 \text{O}_3$. (*Ann. Ch. et Ph.*, Feb., 1846.)

PHOSPHOROUS ACID. PO_3 . The volatile white substance above mentioned as one of the products of the combustion of phosphorus in rarefied

air, consists chiefly of this acid in a dry state: by burning phosphorus in a tube with very limited access of air, and caution as to temperature, as for instance, by placing a piece of phosphorus near one end of a tube three feet long, inflaming it, and gently propelling air through the tube, it may be collected in the form of a white volatile powder, which, when exposed to air, rapidly absorbs moisture, becomes hot, inflames, and burns into phosphoric acid. Heated in close vessels it gives off phosphorus and leaves phosphoric acid. It rapidly dissolves in water, has a sour taste, reddens vegetable blues, and combines with certain of the salifiable bases to form salts called *phosphites*. When acted upon by such of the metallic oxides as readily part with their oxygen, it is converted into phosphoric acid.

The phosphorous acid in combination with a definite proportion of water, forming what Sir H. Davy termed *hydrophosphorous acid*, is obtained (1) by mixing *terchloride of phosphorus* with water: a mutual decomposition of the liquids ensues, and hydrochloric acid and phosphorous acid result; the former is easily driven off by heat, and, on carefully evaporating the remaining solution, a crystallizable compound is obtained, of a sour taste, and very soluble in water, which by heat is resolved into phosphoric acid and phosphuretted hydrogen. (2). A current of chlorine passed through phosphorus fused under hot water, first converts it into a chloride, which afterwards reacts on the water: on evaporation, the hydrophosphorous acid remains.

The slow and spontaneous combustion of phosphorus in a moist atmosphere, as when phosphorus is suffered to deliquesce upon a funnel, is attended by the gradual production of a sour liquid, which appears to be a mixture of hydrated phosphorous and phosphoric acids. Dulong termed it *phosphatic acid*. It is also formed by subjecting phosphorus to the joint action of air and water: and if, in this way, the access of air be limited, the portion of the phosphorus exposed gradually disappears, and little else than phosphorous acid is found in solution.

Anhydrous phosphorous acid consists of

	1	1				Dulong.	Davy.	Berzelius.			
Phosphorus	1	32	57·14	57·18	56	56·524
Oxygen	3	24	42·86	42·82	44	43·476
<hr/>											
Phosphorous acid	1		56		100·00		100·00		100		100·000

The crystallized hydrated phosphorous acid contains 3 equivalents of water: $=\text{PO}_3, 3\text{HO}$. Wurtz regards it as containing elementary hydrogen, and assigns to it the formula $\text{PHO}_4, 2\text{HO}$; he considers it as a bibasic acid, and represents the neutral phosphites by the formula $2\text{MO}, \text{PHO}_4$.

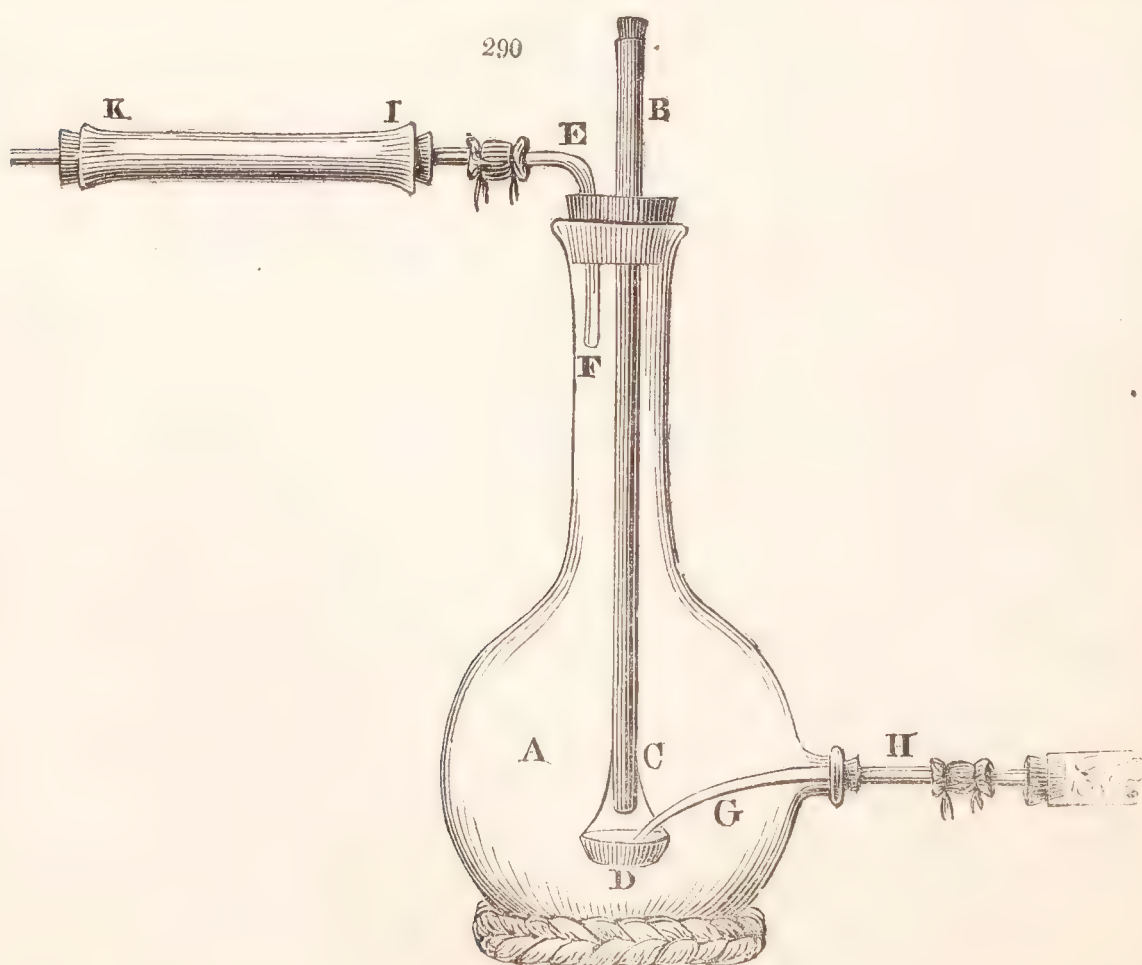
The normal *phosphites* contain, according to Graham, 3 atoms of base to 1 of acid, the hydrated acid being the tribasic phosphite of water. The affinity of the phosphorous acid for bases is but feeble, and it acts in many cases as a reducing agent upon metallic oxides. All the phosphites include water, and when sufficiently heated, are resolved into hydrogen and phosphates, often with combustion. At common temperatures they do not absorb oxygen from the air, but they are easily convertible into phosphates by nitric acid, and other oxidizers.

PHOSPHITE OF AMMONIA. This salt is obtained in deliquescent pris-

matic crystals by saturating phosphorous acid with carbonate of ammonia. When heated it gives out ammonia, and leaves phosphorous acid and water, which, on the further application of heat, is decomposed, and hydrated phosphoric acid remains. (Rose, *Poggend.* ix. 28.) Phosphite of ammonia cannot be dried in vacuo without loss of ammonia, and when heated to 212° it loses, besides ammonia, about 13 per cent., or two equivalents of water. Wurtz represents this salt by the formula $\text{PHO}_4, 2\text{NH}_4\text{O} + 2\text{HO}$.

PHOSPHORIC ACID. PO_5 . Anhydrous phosphoric acid can only be obtained by the direct combustion of phosphorus in excess of dry oxygen; intense heat and light are evolved, and white deliquescent flocculi line the interior of the receiver. It is produced in the same way by burning phosphorus under a dry bell-glass in atmospheric air. For this purpose, a piece of phosphorus, in a platinum or porcelain capsule, may be placed upon a plate of glass, and covered over with a tall receiver; when inflamed, it burns at first furiously, but the combustion gradually subsides for want of oxygen, and may be renewed by gently lifting the receiver off the glass plate: thus the whole of the phosphorus may be gradually burned, and it forms a quantity of dense smoke, which subsides in the form of white flakes.

For the preparation of this anhydrous phosphoric acid upon a larger scale, the following directions are given by Berzelius: Provide a large tubulated flask A (fig. 290), the neck of which is fitted by a tight cork, through which pass two tubes: the one BC of porcelain, reaching to



within about 2 inches of the bottom, the upper end, B, being fitted with a cork, and having attached to its lower end, by platinum wire, the small porcelain cup D: the other tube EF is of glass and bent as shown in the

figure. Another glass tube, GH , is introduced air-tight through the tubulure so as to direct a stream of air into the cup D , the other end being connected with a long tube filled with fragments of chloride of calcium or other material fit for drying the ingressing air. The end E of the upper tube is connected with a larger tube IK , the other end of which communicates with a sucking apparatus; (that is, with the upper stop-cock c of the water-holder, D , as shown in fig. 270, p. 310) in this way fresh and dried air is drawn through the tube GH into the phosphoric acid apparatus, and passes through it and out by the tube EF , a little loose cotton being placed before the cork at K . The flask being thus filled with dry air, pieces of well dried phosphorus are dropped into the cup D through the tube BC , which admits of their being inflamed by a hot wire or glass rod, and is then immediately closed by its cork: the sucking apparatus being put into action, the phosphorus burns into phosphoric acid, and fresh portions are from time to time dropped into the cup, which is generally hot enough to ensure their inflammation without the aid of the hot wire. The phosphoric acid collects in the flask, and any portion which passes on with the current of air, is stopped in the larger tube IK . The product of phosphoric acid is to be transferred as quickly as possible into a dry stopper-bottle, in which it may be pressed down: and the portions of acid which remain adhering to the flask and cup may be washed out, and yield a solution of the acid.

In this anhydrous state phosphoric acid is an extremely deliquescent uncrystalline powder, fusible into a vitreous substance and volatile at a high red heat (DAVY). It is inodorous, very sour, but not corrosive. At high temperatures it is decomposed by charcoal, and by several of the metals. It consists of

						Dulong.	Berzelius.	Davy.		
Phosphorus	1	...	32	...	44·4	...	43·9	...	42·6
Oxygen	5	...	40	...	55·6	...	56·1	...	57·4
<hr/>										
Phosphoric acid	1		72		100·0		100·0		100·0

We are indebted to Professor Graham for an elaborate inquiry into the modifications and peculiarities of phosphoric acid, and the constitution of the phosphates (*Phil. Trans.* 1833, 253) and to L. Gmelin for a clear and connected exposition of the views which have been entertained respecting them. (*Handbuch.*) Phosphoric acid occurs in three peculiar or isomeric conditions, which may be designated, 1. Metaphosphoric acid, or *a* phosphoric acid; aPO_5 : 2. Pyrophosphoric acid, or *b* phosphoric acid; bPO_5 : 3. Common phosphoric acid, or *c* phosphoric acid; cPO_5 . The first combines with *one*, the second with *two*, and the third with *three* atoms of base. The acid itself is regarded by Graham as the same in all these modifications, which are supposed to depend upon the proportion of water or base with which it is in union: so that aPO_5 may become bPO_5 by the acquisition of a second atom of water or of base, and cPO_5 by a third; and inversely cPO_5 by losing an atom of base or of water, becomes bPO_5 , and this by the further abstraction of base or basic water passes into aPO_5 , and aPO_5 , losing its single equivalent of water or base reverts to PO_5 . Gmelin observes that these modifications may be either isomeric or polymeric: the arrangement of the atoms of phosphorus and oxygen appearing to be modified by the number of the

atoms of water or base, so as to constitute acids having different capacities of saturation: or, according to Graham, phosphoric acid intimately combined with one atom of water, only allows of the replacement, by substitution, of that atom of water by one atom of base: but if the original acid be similarly united with 2 or 3 atoms of water, these are then replaced by 2 or 3 atoms of base.

$a\text{PO}_5, \text{HO}$. *Protohydrate of Phosphoric Acid. Monobasic Phosphate of Water. Metaphosphoric Acid.* Aqueous solutions of any of the modifications of phosphoric acid when evaporated and heated, till they cease to lose water, yield this protohydrate, in the form of what has been termed *glacial phosphoric acid*. When biphosphate of soda is heated to redness, dissolved in water, precipitated by acetate of lead, and the precipitate treated by sulphuretted hydrogen, an acid liquor is obtained which is a solution of the protohydrate: it is characterized by producing a white precipitate in solution of albumen; and in solutions of baryta, lime, and oxide of silver, it gives peculiar white precipitates like soft solids without crystallization. These all contain 1 atom of base to 1 of acid. This acid contains

Phosphoric acid.....	1	72	88.8	Peligot. 87.45
Water	1	9	11.2	12.55
<hr/>							
Metaphosphoric acid.....	1		81		100.0		100.00

$6\text{PO}_5, 2\text{HO}$. *Deutohydrate of Phosphoric Acid, or Bibasic Phosphate of Water. Pyrophosphoric Acid. Paraphosphoric Acid.* When a solution of pyrophosphate of soda is precipitated by acetate of lead, and the insoluble salt of lead washed and decomposed by sulphuretted hydrogen, an acid liquor is obtained, which must be left in a shallow basin till the sulphuretted hydrogen has escaped: it is then an aqueous solution of pyrophosphoric acid: it yields the pyrophosphate when neutralized by carbonate of soda; gives a *white* precipitate with nitrate of silver; and forms salts all of which have 2 atoms of base. A dilute solution of this deutohydrate of phosphoric acid may be preserved without change, but when boiled for some time it passes into terhydrate. Graham and Peligot obtained this acid, not however quite free from terhydrate, by evaporating the solution of the terhydrate in a platinum flask till its temperature attained 416° . It appeared as a soft glass. Peligot obtained it in opaque imperfect crystals resembling grape sugar: it may be represented as containing

Phosphoric acid	1	72	80	Peligot. 77
Water	2	18	20	23
<hr/>							
Pyrophosphoric acid	1		90		100		100

$c\text{PO}_5, 3\text{HO}$. *Terhydrate of Phosphoric Acid, or Tribasic Phosphate of Water. Common Phosphoric Acid.* The common phosphate of soda of pharmacy may be resorted to for this hydrate of phosphoric acid, but it should be previously purified by recrystallization: it may be decomposed by acetate of lead, and the resulting precipitate of phosphate of lead washed, suspended in water, and decomposed by a stream of sulphuretted hydrogen gas, the excess of which is then expelled by heat, and the liquor filtered: it is very sour, and contains the terhydrate of

phosphoric acid. The characters of this acid solution are to give a *yellow* precipitate with nitrate of silver, to yield the common phosphate of soda when neutralized with carbonate of soda, to form salts which have invariably 3 atoms of base to 1 of acid, and to be unalterable by boiling its solution or keeping it for any length of time. (GRAHAM.) The solution of this terhydrate evaporated to the consistency of thin syrup and set aside, yields crystals in the form of flat six-sided prisms: evaporated in vacuo over sulphuric acid, it forms thin deliquescent plates: heated to 400° it becomes a mixture of the deuto and proto-hydrates, and by heating it carefully to redness, it may be converted into protohydrate: it consists of

					Brandes.	Peligo.
Phosphoric acid	1	72	72.72	72.205	71.6	
Water	3	27	27.28	27.795	28.4	
<hr/>						
Terhydrated phosphoric acid	1	99	100.00	100.000	100.0	

Phosphates. Graham has shown that each of the above hydrates of phosphoric acid forms a distinct class of salts, namely, *metaphosphates*, which are monobasic; *paraphosphates* or *pyrophosphates*, which are bibasic; and *common phosphates*, which are tribasic; so that the proportion of fixed base with which the acid unites in the humid way is dependent upon the proportion of water which the fixed base replaces. Thus, the metaphosphoric acid, or protohydrate, will only combine with one, and the paraphosphoric or deutohydrate with two equivalents of soda; and if in either case a larger quantity of base be added, it remains uncombined: so also in regard to the terhydrate; if to one equivalent of it in solution one equivalent of soda be added, one equivalent only of its water is displaced and two are retained: $3\text{HO}, \text{PO}_5 + \text{NaO} = \text{NaO}, 2\text{HO}, \text{PO}_5 + \text{HO}$. On the addition of a second equivalent of soda, a second atom of basic water is displaced, the salt therefore still remaining characteristically tribasic; for in this case, $\text{NaO}, 2\text{HO}, \text{PO}_5 + \text{NaO}$, becomes $2\text{NaO}, \text{HO}, \text{PO}_5 + \text{HO}$; and, lastly, the addition of a third equivalent of soda displaces the remaining atom of water, and we have an anhydrous tribasic phosphate of soda: $2\text{NaO}, \text{HO}, \text{PO}_5 + \text{NaO} = 3\text{NaO}, \text{PO}_5 + \text{HO}$. So also in regard to the insoluble phosphates formed by precipitation: the monobasic or metaphosphate of soda, decomposes 1 equivalent of nitrate of silver, and a white monobasic phosphate of silver is thrown down: $\text{NaO}, \text{PO}_5 + \text{AgO}, \text{NO}_5 = \text{AgO}, \text{PO}_5 + \text{NaO}, \text{NO}_5$. On the other hand, the bibasic salt, or pyrophosphate of soda, decomposes 2 equivalents of nitrate of silver to form a white bibasic phosphate of silver: $2\text{NaO}, \text{PO}_5 + 2[\text{AgO}, \text{NO}_5] = 2\text{AgO}, \text{PO}_5 + 2[\text{NaO}, \text{NO}_5]$. And, lastly, 1 equivalent of the common or tribasic phosphate of soda decomposes 3 equivalents of nitrate of silver, forming 1 equivalent of the yellow or common phosphate of silver, and 3 of nitrate of soda. $3\text{NaO}, \text{PO}_5 + 3[\text{AgO}, \text{NO}_5] = 3\text{AgO}, \text{PO}_5 + 3[\text{NaO}, \text{NO}_5]$.

If nitrate of lead be substituted in the above cases for nitrate of silver, corresponding phosphates of lead are formed, and if these be diffused in water, and decomposed by sulphuretted hydrogen, they respectively afford solutions of the protohydrate, deutohydrate, and terhydrate of phosphoric acid: thus, $\text{PbO}, \text{PO}_5 + \text{HS} = \text{PbS} + \text{HO}, \text{PO}_5$ giving the protohydrated, or metaphosphoric acid: and again, $2\text{PbO}, \text{PO}_5 + 2\text{HS} = 2\text{PbS} + 2\text{HO},$

PO_5 , in which 1 equivalent of pyrophosphate of lead decomposes 2 of sulphuretted hydrogen, forming 2 of sulphuret of lead and one of deutohydrated phosphoric acid: and, lastly, $3\text{PbO}, \text{PO}_5 + 3\text{HS} = 3\text{PbS}, + 3\text{HO}$, PO_5 , when the tribasic phosphate of lead decomposes 3 equivalents of sulphuretted hydrogen, throwing down 3 of sulphuret of lead, and leaving in solution 1 equivalent of the terhydrated acid.

In regard to these decompositions, there is no transition from one species of phosphate to another, because the decompositions are mutual, and the products neutral; but there are conditions, under which these transitions do ensue: these are described by Graham as follows:

1st. *Changes without the intervention of high temperatures.* When aqueous solutions of the protohydrate and deutohydrate of phosphoric acid are warmed, they gradually pass into terhydrate, or common acid, and the metaphosphate of water appears at once to become common phosphate, without passing through the intermediate state of hydration of the pyrophosphate; the insoluble metaphosphate of baryta, when boiled in water, gradually becomes common phosphate, which is soluble.

2. *Changes with the intervention of a high temperature.* If a single equivalent of phosphoric acid, anhydrous, or in any state of hydration, be heated to a little below redness with a single equivalent of soda or its carbonate, the *metaphosphate* is formed; with 2 equivalents, the *pyrophosphate*; and with 3, the *common phosphate*; hence the formation of none of those classes is peculiarly the effect of a high temperature. Again, a tribasic phosphate containing 1 or 2 equivalents of a volatile base, such as water or ammonia, loses the volatile base when ignited, and the acid remains in combination with the fixed base. Hence common phosphate of soda, $(\text{HO}, 2\text{NaO}, + \text{PO}_5)$ is converted by heat into pyrophosphate $(2\text{NaO} + \text{PO}_5)$ according to the original observation of Dr. Clark; and the biphosphate of soda, $(2\text{HONaO}, + \text{PO}_5)$ into metaphosphate of soda $(\text{NaO} + \text{PO}_5)$. The acid remains in combination with the fixed base left with it, and the salt produced may be dissolved in water, without assuming basic water.

The metaphosphate of soda is susceptible of a remarkable conversion by the agency of a certain temperature, and exhibits a change of nature without a change of composition such as often occurs in organic compounds, but rarely admits of so satisfactory an explanation. This particular salt, in common with all the other phosphates, combines with water which becomes attached to the salt in the state of constitutional water, or water of crystallization. The metaphosphate of soda so hydrated, when dried at 212° , retains one equivalent of water, but that water is not *basic*, for on dissolving the salt again, it is found still to be a metaphosphate; but, let this hydrated metaphosphate be heated to 300° , and without losing anything, it changes completely, and becomes a pyrophosphate, the water which was constitutional before being now basic. The formulæ of the salt in its two states exhibit to the eye the nature of the internal change which has occurred in it.

1. Hydrated Metaphosphate of soda $\text{NaO}, \text{PO}_5 + \text{H}_2\text{O}$

2. Pyrophosphate of soda and water $\text{NaO}, \text{HO} + \text{PO}_5$.

In the preceding details respecting the phosphates and their acids, I have followed Graham: another view of their constitution has also been proposed, in which the three acids, instead of being regarded as hydrates

of the same anhydrous acid, are considered as *distinct hydracids*, formed that is of hydrogen united in each to a distinct compound radical, the monobasic acid being $H + PO_6$; the bibasic acid $H_2 + PO_7$, and the tribasic acid, $H_3 + PO_8$. In the formation of the salts of these acids, it is assumed that H is replaced by M , in the same way as upon the ordinary hypothesis HO is replaced by MO . Thus the common or tribasic phosphate of soda, instead of being represented by $HO, 2 NaO + PO_5$, would have the formula $H, Na_2, + PO_8$. Dr. Gregory, in expounding this hypothesis (*Outlines of Chemistry*, p. 112,) observes that, "if we represent the common or tribasic phosphate of soda by

$$PO_8 = \begin{cases} \frac{1}{3}PO_8 + Na \\ \frac{1}{3}PO_8 + Na, \\ \frac{1}{3}PO_8 + H \end{cases}$$

then, when this salt is ignited 1 equivalent of hydrogen is expelled along with 1 equivalent of oxygen, and the 2 equivalents of sodium now neutralize the whole of the remaining phosphorus and oxygen, which is $\frac{2}{3}PO_8 - O = PO_7$, and the bibasic salt $2 Na + PO_7$ results. If this be expressed by

$$PO_7 = \begin{cases} \frac{1}{2}PO_7 + Na, \\ \frac{1}{2}PO_7 + Na, \end{cases}$$

we see that something has been added to the radical previously united with each equivalent of sodium, without altering its neutralising power. In like manner, if we represent microcosmic salt (tribasic ammonia phosphate of soda = $NaO, NH_4O, HO, + PO_5$, or)

$$= PO_8 \begin{cases} Na \\ NH_4 \\ H \end{cases} \text{ as follows: } PO_8 = \begin{cases} \frac{1}{3}PO_8 + Na \\ \frac{1}{3}PO_8 + NH_4, \\ \frac{1}{3}PO_8 + H \end{cases} \text{ we see, that}$$

when it is ignited the hydrogen and ammonium are both expelled, each combined with 1 equivalent of oxygen; but as the rest of the phosphorus and oxygen formerly combined with them is not expelled, it enters into composition of the radical still united with 1 equivalent of sodium, but without affecting its neutralising power: this radical, therefore, becomes $\frac{2}{3}PO_8 - O_2 = PO_6$; and its salt with sodium is PO_6, Na , the monobasic phosphate of soda.

If we now turn to the acids of sulphur, viewed as hydrogen acids, we shall there see many analogous cases of the addition to the acid radical of different quantities of its elements, while the neutralising power remains unchanged. Thus, hydrated sulphurous acid, $= H + SO_3$, by the addition of $SO_3 + S_2$ to its radical, becomes the acid of Fordos and Gélis, without change of neutralising power. In the phosphoric acids the neutralising power varies because the hydrogen varies; but when they are represented, as above, in such a way as to keep the hydrogen (or metal) the same in all, the analogy between them and the acids of sulphur, in regard to the non-dependence of the neutralising power on the nature and proportions of the ingredients of the radical, becomes manifest." In this quotation I have substituted P for P_2 , the latter being the symbol of the equivalent of phosphorus adopted by Dr. Gregory.

PHOSPHATE OF AMMONIA. TRIBASIC PHOSPHATE OF OXIDE OF AMMONIUM AND WATER. $2(NH_4O) HO, PO_5$ or $2 NH_3, 3 HO, PO_5$.

(*Common Phosphate.*) The mutual action of anhydrous phosphoric acid and ammonia has not been studied: they probably give rise to an *amide*. The above tribasic phosphate, formerly called the *neutral phosphate of ammonia*, may be obtained pure by saturating a solution of phosphoric acid with ammonia or carbonate of ammonia and carefully evaporating, so as to avoid the production of an acid salt. It may also be formed by adding carbonate of ammonia to the acid phosphate of lime obtained from bone earth (p. 413,) till no further effervescence or precipitation of phosphate of lime follows, filtering and evaporating, taking care, however, to leave slight excess of ammonia: the solution left to itself deposits the salt. Its primary form is an oblique rhombic prism, the smaller angle of which is $84^{\circ} 30'$. Its prisms are often terminated by dihedral summits. (MITSCHERLICH, *Ann. Ch. et Ph.*, xix. 382; BROOKE, *Ann. Phil.*, xxii. 285.) The crystals are efflorescent, and by exposure to air lose part of their ammonia; they taste saline, cooling, and bitterish. This salt is soluble in 4 parts of cold water: it is insoluble in alcohol. When heated it melts, and losing ammonia leaves hydrated phosphoric acid. It exists, combined with phosphate of soda and of magnesia, in the urine of carnivorous animals. The components of this salt are

												Mitscherlich.			
Ammonia2	34	25	57	}	=	{	Oxide of ammonium2	52	39	11			
Water3	27	20	30				Water1	9	6	76			
Phosphoric acid1	72	54	13				54	42	Phosphoric acid1	72	54	13	
<hr/>					<hr/>					<hr/>					
Tribasic phosphate of ammonia (common)					}					1	133	100	00		

TRIBASIC PHOSPHATE OF WATER AND OXIDE OF AMMONIUM. 2HO , NH_4O , PO_5 , or 3HO , NH_3PO_5 . (*Biphosphate.*) This salt is obtained by adding phosphoric acid to a solution of the phosphate of ammonia till it strongly reddens litmus paper, and ceases to occasion a precipitate in a dilute solution of chloride of barium. When the solution is concentrated it yields crystals, the primary form of which is an octohedron with a square base; but they are most commonly right square prisms terminated by the primary faces. They are less soluble than the preceding salt, and permanent in the air: when heated they fuse and froth up, ultimately leaving hydrated phosphoric acid. They consist of

Mitscherlich.														
Water3	27	23	28	}	=	{	Water2	18	15	52		
Ammonia1	17	14	65				Oxide of ammonium1	26	22	41		
Phosphoric acid1	72	62	07				61	02	Phosphoric acid1	72	62	07
<hr/>					<hr/>					<hr/>				
Tribasic phosphate of ammonia (biphosphate)					}					1	116	100	00	

The *monobasic* and *bibasic phosphates of ammonia* (metaphosphate and pyrophosphate) are only known in aqueous solution: the former passing on evaporation into 2HO , NH_4O , PO_5 ; and the latter into the common phosphate $= 2\text{NH}_4\text{O}$, HO , PO_5 . (GRAHAM.)

Gay Lussac has recommended the application of phosphate of ammonia to render muslin, and similar articles of clothing, to a considerable extent incombustible. The goods are immersed in a solution of equal parts of phosphate and hydrochlorate of ammonia of a due strength, and

then dried; upon applying flame to them, it will be found that they are burned with great difficulty, and cannot be consumed with flame, in consequence of the prevention of the access of oxygen by the glazing which the salts form at high temperatures. The salts may be mixed with the starch, and applied in the usual way to dresses, curtains, and other combustible tissues: many serious accidents might in this way be prevented.

PHOSPHORUS AND CHLORINE.—These elements unite in two proportions, forming two definite compounds, the *protochloride* or *sesquichloride*, and the *perchloride* of phosphorus.

PROTOCHLORIDE OF PHOSPHORUS. SESQUICHLORIDE OF PHOSPHORUS. TERCHLORIDE OF PHOSPHORUS. PCl_3 . This compound is procured by distilling a mixture of phosphorus and *perchloride of mercury*; or, what amounts to the same thing, by passing the vapor of phosphorus over perchloride of mercury in a heated glass tube terminating in a cooled receiver. It is also formed by passing chlorine first through a cold flask, then through a tube containing fragments of fused chloride of calcium, and thence into a tubulated retort, slightly warmed, and containing phosphorus, from which the sesquichloride, as it is formed, gradually distils over into a cooled receiver. (GMELIN.)

When first obtained, this compound generally holds a little phosphorus in solution, which gives it a reddish color; this is in time deposited, and it becomes limpid and colorless; or it may at once be purified by slow distillation; it requires to be cautiously excluded from the action of the air. It has a suffocating odor. Its specific gravity is 1.45. Exposed to the air it exhales acid fumes: it does not change the color of *dry* vegetable blues, but becomes powerfully acid upon the least acquisition of moisture. Its vapor is combustible. Chlorine converts it into perchloride of phosphorus. It acts upon water with great energy, and produces *phosphorous* and hydrochloric acids, as above stated (page 419). $\text{PCl}_3 + 3 \text{HO} = \text{PO}_3 + 3 \text{HCl}$.

It appears from the analysis of Davy and of Berzelius, that this chloride corresponds in composition to the phosphorous acid; it consists of

						Davy & Berzelius.	
Phosphorus	1	32	22.86	23
Chlorine	3	108	77.14	77
<hr/>						<hr/>	
Protochloride of phosphorus	1		140		100.0		100

PERCHLORIDE OF PHOSPHORUS. PCl_5 . When phosphorus is submitted to the action of chlorine in excess, it burns with a pale yellow flame, and produces a white, flaky, and volatile compound, which attaches itself to the interior of the vessel, and which is the *perchloride of phosphorus*. It may be conveniently formed in the exhausted retort, as described at p. 278. It was formerly mistaken for phosphoric acid, but its easy volatility is alone sufficient distinction, for it rises in vapor at 200° . It is fusible under pressure, and crystallizable in transparent prisms; it is a non-conductor of electricity; it reddens dry litmus paper, in consequence, as Berzelius supposes, of its acquiring hydrogen and oxygen from the decomposition of the paper. It fumes in the air, and when brought into the contact of water, a mutual decomposition is im-

mediately effected, and *phosphoric* and hydrochloric acids result. $\text{PCl}_5 + 5\text{HO} = \text{PO}_5 + 5\text{HCl}$. When passed through a red-hot porcelain tube with oxygen, phosphoric acid is produced and chlorine evolved; which shows that oxygen, at that temperature, has a stronger attraction for phosphorus than chlorine. Potassium, heated in its vapor, burns with great brilliancy: with dry sulphuretted hydrogen it yields hydrochloric acid and chlorosulphuret of phosphorus (SERULLAS.) $\text{PCl}_5 + 2\text{HS} = \text{PS}_2\text{Cl}_5 + 2\text{HCl}$. Metallic oxides decompose it with the production of metallic chlorides and phosphates. (DAVY.)

Perchloride of phosphorus consists of

						Davy.	Dulong.	Berzelius.			
Phosphorus	1	...	32	...	15.09	...	13	...	15.4	...	15.31
Chlorine	5	...	180	...	84.91	...	87	...	84.6	...	84.69
<hr/>											
Perchloride of phosphorus	1		212		100.00		100		100.0		100.00

AMMONIA AND CHLORIDE OF PHOSPHORUS. *The action of ammonia on the chlorides of phosphorus* was first examined by Davy, and afterwards by H. Rose. When ammonia is admitted into an exhausted retort containing the perchloride of phosphorus, the gas is rapidly absorbed with much heat, and a compound is produced which, according to Davy, is insoluble in water, indecomposable by acid or alkaline solutions, and has characters analogous to an earth. The action of ammonia on the protochloride is attended by the production of the same compound, and the separation of a portion of phosphorus. (*Elements*, p. 291.) According to H. Rose, the most definite action of ammonia is on the protochloride of phosphorus. (*Poggend.*, xxiv. 308.) This liquid, when freed from dissolved phosphorus by repeated distillation, and subjected (surrounded by a freezing mixture so as to prevent elevation of temperature and consequent deposition of phosphorus) to the gradual action of excess of ammonia, forms with it a perfectly white compound, which is entirely, though very slowly, soluble in water, and is so constituted, as to yield in this process hydrochlorate and phosphite of ammonia. When heated in the air, it gives off hydrochlorate of ammonia, and leaves an insoluble reddish-brown substance, which, when heated, becomes white, but again brown as it cools. To obtain this fixed residue in a pure state, freshly prepared *ammonio-protochloride of phosphorus* must be cautiously heated to redness out of the contact of air: this is best done by putting it into a sufficiently large tube of difficultly fusible glass, and passing over it at a red heat a stream of carbonic-acid gas dried by contact of chloride of calcium: the operation must be patiently carried on till no traces of hydrochlorate of ammonia are evolved. With these precautions, the substance which remains is a light white powder, and though formed of highly-volatile substances is, when excluded from air and moisture, fixed and infusible at a red heat; heated in contact of the air and its moisture, it evolves white fumes of phosphoric acid, and becomes slowly oxidized without flaming: if thus heated in a platinum crucible, the metal is much corroded. Exclusively of its fixedness out of the contact of air, the most remarkable property of this substance is its indifference to the strongest re-agents. Concentrated nitric acid very slowly converts a portion of it into phosphoric acid, and concentrated sulphuric acid produces the same change with the

evolution of sulphurous acid; but the dilute acids and alkaline solutions, and chlorine, sulphur, and carbonic acid, have no action upon it even when heated. It is, on the contrary, energetically acted upon when fused with caustic potassa: ammonia is evolved, and the residue is soluble in water. It is decomposed when heated with hydrate of baryta, with intense ignition: it is also decomposed by fusion with the carbonated fixed alkalis, and with their nitrates. The action of dry hydrogen gas upon this compound at a red heat is very remarkable; no trace of water is formed, phosphorus is evolved, and distils off, and on conducting the gaseous products into water, ammonia is found in solution. From this result, and from other evidence adduced by Rose, this compound consists of phosphorus and nitrogen; and from the analytical details given at length in the essay I have quoted, it appears that 100 parts of the ammonio-chloride yield an average product of 21.27 of this phosphuret of nitrogen, and that it consists of

						Rose.	Wöhler & Liebig.
Phosphorus	1	32	53.3 52.56 51
Nitrogen	2	28	46.7 47.44 49
<hr/>							
Phosphuret of nitrogen	1		60		100.0	100.00	100

Phosphuret of nitrogen is also produced, according to Wöhler and Liebig (*Ann. der Pharm.*, xi. 139) by passing vapor of protochloride of phosphorus over sal ammoniac heated up to its point of vaporization: hydrochloric acid and phosphorus are evolved, and phosphuret of nitrogen remains in white and brown flocculi ($2\text{PCl}_3 + 2\text{NH}_4\text{Cl} = \text{N}_2\text{P} + 8\text{HCl} + \text{P}$.) If perchloride of phosphorus be used, the resulting phosphuret retains traces of chlorine and hydrogen after long ignition in carbonic acid.

HYDRATED PHOSPHURET OF NITROGEN. $\text{PN}_2, 2\text{HO}$. When perchloride of phosphorus is saturated with ammoniacal gas, and the resulting product washed with water, boiled with solution of potassa, and lastly with dilute nitric acid (for the purpose of removing all traces of sal ammoniac,) a white powder remains, composed of

						Wöhler & Liebig.
Phosphorus	1	32	41.04 40.68
Nitrogen	2	28	35.89 35.05
Water	2	18	23.07 24.27
<hr/>						
Hydrated phosphuret of nitrogen....	1		78		100.00	100.00

CHLOROPHOSPHURET OF NITROGEN. $\text{N}_2, \text{P}_3, \text{Cl}_5$. This compound also results from the action of perchloride of phosphorus on ammonia or sal ammoniac. 1. Perchloride of phosphorus is saturated with undried ammoniacal gas, and the resulting white mass distilled with water: crystals condense in the water of the receiver, which are to be washed, dried, and purified by solution in warm ether and crystallization. 2. Perchloride of phosphorus is introduced into the sealed end of a glass tube three feet long, and at a little distance from it long pieces of sal ammoniac, so as to half fill the tube; the part containing the sal ammoniac is then heated in a long horizontal furnace till the salt begins to rise in vapor; the perchloride is then gently heated so as to send its vapor slowly over the sal ammoniac;

hydrochloric acid gas is evolved, and crystals of chlorophosphuretted nitrogen condense in the cold part of the tube: these are washed and purified as before. The crystals are regular six-sided prisms, brittle, and repel water like greasy bodies: they fuse below 212° , and at higher temperatures sublime unaltered. When gently heated, their odor is peculiar but not acrid: they are soluble in alcohol and ether; they are not acted upon by hydrochloric, nitric, or sulphuric acid, nor by solution of potassa; when heated with these liquids they collect like oil upon the surface and sublime. (WÖHLER and LIEBIG. *Ann. der Pharm.*, xi. 146. L. GMELIN. *Handbuch*, I. 884.) They consist of

						Wöhler & Liebig.	
Nitrogen	2	...	28	...	9.21	...	10.3
Phosphorus	3	...	96	...	31.58	...	31.4
Chlorine	5	...	180	...	59.21	...	58.3
<hr/>						<hr/>	
Chlorophosphuret of nitrogen.....	1		304		100.00		100 0

PHOSPHORUS AND IODINE. These bodies readily combine at common temperatures, and produce *iodides of phosphorus*, varying in color from blackish-brown to orange-yellow according to the preponderance of one or other element. 1 of phosphorus and 24 of iodine yield a black mass fusible at 114° , and giving a brown solution in water: 1 of phosphorus and 16 of iodine is a grey crystalline compound, fusible at 84° , and forming with water phosphorous and hydriodic acids: 1 of phosphorus and 8 of iodine give an orange-yellow mass fusible at 212° , and resolved by water into phosphorous and hydriodic acids, and phosphuretted hydrogen, whilst flakes of phosphorus are deposited. (GAY LUSSAC.)

There are probably three iodides of phosphorus: 1. Yielding hydriodic and hypophosphorous acids, when decomposed by water, and therefore = PI. 2. Giving with water hydriodic and phosphorous acids, and therefore = PI₃. 3. Producing with water hydriodic and phosphoric acid, and hence = PI₅. (KANE.) These compounds require further examination.

	PI				PI ₃				PI ₅						
Phosphorus...	1	...	32	...	20.3	1	...	32	...	7.8	1	...	32	...	4.9
Iodine	1	...	126	...	79.7	3	...	378	...	92.2	5	...	630	...	95.1
	<hr/>				<hr/>				<hr/>						
	1		158		100.0	1		410		100.0	1		662		100.0

PHOSPHORUS AND BROMINE. There are two bromides of phosphorus. When phosphorus and bromine are mixed in a flask filled with carbonic acid, they act intensely upon each other: heat and light are evolved, and a yellow crystalline substance rises to the upper part of the flask, whilst a liquid remains at the bottom. The latter is the *terbromide*; it is volatile, and emits pungent fumes when exposed to air. Water resolves it into hydrobromic and phosphorous acids. The crystalline *perbromide* is converted, by a gentle heat, into a red liquid, and at a higher temperature into red vapor. It emits fumes when exposed to air, and, acted upon by water, forms hydrobromic and phosphoric acid. Both these bromides are decomposed by chlorine, with the evolution of bromine and the formation of chloride of phosphorus. Iodine, on the contrary, does not decompose them; but bromine decomposes the iodides of phosphorus. (BALARD.)

Much caution is requisite in adding phosphorus to bromine, in consequence of the explosive violence with which they combine. Rose recom-

mends the phosphorus to be put into a small tube open at one end, so as to allow the bromine vapor only to act upon it. When the liquid has lost its color, it may be distilled from excess of phosphorus. Faraday also observes that the bromides of phosphorus are easily made without risk of explosion: if a glass tube be bent so as to have two depressions, phosphorus placed in one and bromine in the other, then by inclining the tube the vapor of bromine can be made to flow gradually on to, and combine with, the phosphorus. The fluid protobromide is first formed, and this is afterwards converted into the solid perbromide: the excess of bromine may be dissipated by the careful application of heat. (*Phil. Trans.*, 1845, 161.) Bromide of phosphorus may also be formed by passing phosphorus in vapor over bromide of mercury. This compound (PBr_3) is a colorless volatile liquid fuming in the air, and reddening damp litmus paper: it does not congeal at 15° . (LÖWIG.) It consists of

Phosphorus	1	...	32	...	12.03	...	Löwig. 11.7
Bromine	3	...	234	...	87.97	...	88.3
<hr/>							
Terbromide of phosphorus.....	1		266		100.00		100.0

Balard's crystalline perbromide may also be obtained by the addition of 2 atoms of bromine to the terbromide. It is composed of

Phosphorus	1	...	32	...	7.58	...	Löwig. 6.8
Bromine	5	...	390	...	92.42	...	93.2
<hr/>							
Perbromide of phosphorus	1		422		100.00		100.0

FLUORIDE OF PHOSPHORUS. By distilling fluoride of lead or mercury with phosphorus, Davy obtained a fuming liquid, resolved by the action of water into hydrofluoric and phosphorous acids: hence $=\text{PF}_3$. (DUMAS, *Ann. Ch. et Ph.*, XXXI. 435.)

PHOSPHORUS AND HYDROGEN; PHOSPHURETTED HYDROGEN; HYDRURET OF PHOSPHORUS. PH_3 . Phosphorus may be heated and even sublimed, in hydrogen gas, without the formation of any definite compound, although, under such circumstances, the gas retains a portion of the vapor of phosphorus, acquiring its peculiar odor, and becoming luminous in the dark when mixed with atmospheric air. When phosphorus is presented to *nascent* hydrogen, two gaseous compounds result. They appear to be similar in composition, but one is spontaneously inflammable on coming into contact of air at common temperature and pressure, whereas the other only inflames at higher temperature or under a diminished pressure. The first variety may be procured by heating phosphorus in a solution of caustic potassa; or by acting upon *phosphuret of lime* by dilute hydrochloric acid. In the former case about a quarter of an ounce of phosphorus should be introduced into a small retort, capable of holding about four ounces of water; it should then be completely filled with a moderately-strong solution of potassa, and the beak being placed under the shelf of the pneumatic apparatus, the heat of an Argand lamp carefully applied till it boils: gas will gradually be generated, so as to expel a portion of the alkaline solution, and ultimately to bubble up through the water. Upon coming into contact with the air, the bubbles

inflammes with a slight explosion; and if the atmosphere is still, each as it bursts produces a beautifully-expanding ring of smoke, in consequence of the sudden formation of phosphoric acid and water. If the retort, in which the gas is generated, contain common air, the first bubbles burn within the vessel, and the retort is frequently broken by the percussion, or by the rush of cold water from the trough, caused by the sudden expansion and subsequent contraction of the air within: an accident prevented by filling the retort with the liquid, or by previously displacing part of the alkaline solution by hydrogen or nitrogen gas.

For obtaining this gas by the second process, Dr. Thomson gives the following directions:—Fill a small retort with water acidulated by hydrochloric acid, and then throw into it a quantity of phosphuret of lime in lumps. Plunge the beak of the retort under water, and place over it an inverted jar filled with that liquid. Phosphuretted hydrogen gas is extricated in considerable quantity, and soon fills the glass jar. Half an ounce of phosphuret of lime yields about 70 cubic inches of this gas. (*Inorg. Chem.*, i. 251.) Dumas obtains it by introducing a little water into an inverted jar filled with and standing over mercury, and then throwing up portions of powdered phosphuret of barium or calcium, wrapped in filtering paper: the reaction is rapid at first, but continues slowly for some hours. (*Ch. App. aux Arts*, i. 265.) It may also be obtained by heating a mixture of 1 part of phosphorus, 16 of hydrate of lime, and 4 of water. (RAYMOND, *Ann. de Chim.*, x. 19.)*

This gas was discovered by Gengembre in 1783; it is colorless, has a nauseous odor like onions, or, according to some, resembling that of putrid fish, a bitter taste, and inflames when mixed with air, a property which it loses by being kept over water: water takes up about two *per cent.* of this gas, and acquires a bitter taste, and the smell of onions; but the solution has no acid properties like that of sulphuretted hydrogen. When the gas is retained in dry vessels, or over mercury, and carefully excluded from light, it may be kept some time without alteration: but, in the contact of water, and exposed to light, it soon deposits a red film, without changing its volume, and loses the property of spontaneous inflammability. It has been asserted, that in this case the gas deposits half of its phosphorus, and that a definite *subphosphuretted hydrogen* remains; but this statement requires further proof. Houton Labillardière has remarked, that bubbles of phosphuretted hydrogen sent up into a portion of common air standing over mercury, do not inflame when the air is compressed, or when the mercury is at the same level within and without the vessel; but that explosion immediately ensues when the confined air is rarefied by lifting up the jar, so that the column of mercury within may be above that without. When bubbles of phosphuretted hydrogen are sent up into a jar of oxygen, they burn with greatly increased splendor; in chlorine, too, they burn with a beautiful pale blue light, forming hydrochloric acid and perchloride of phosphorus. In a narrow tube it may be mixed with oxygen without exploding, in which case it is

* Faraday succeeded in liquifying the phosphuretted hydrogen gas obtained by boiling phosphorus in solution of caustic potassa: it condensed into a limpid fluid under high pressure in the carbonic acid bath: it could not be solidified: a portion of uncondensable gas (hydrogen?) always remained (*Phil. Trans.*, 1845, 162).

deprived of its phosphorus. It burns when thrown up into nitrous oxide.

In the experiment of throwing up bubbles of this gas into a jar of oxygen, it often happens that several do not inflame, and if after this, one passes up and inflames, its explosion may endanger the vessel: this may be prevented by adding a trace of chlorine to the oxygen, by which the inflammation of each gas bubble is generally ensured.

The second modification of phosphuretted hydrogen, which at common temperatures and pressures is not spontaneously inflammable, was discovered by Sir H. Davy, in 1812. It is procured by heating the solid *hydrate of phosphorous acid*, or *hydrophosphorous acid* (p. 419), in a small retort. $4[3\text{HO}, \text{PO}_3] = \text{PH}_3, 9\text{HO}, 3\text{PO}_5$. The gas must be collected over mercury, for water absorbs one-eighth its volume. It is also formed, according to Dumas, by the action of strong hydrochloric acid on phosphuret of calcium. It is not spontaneously inflammable, but explodes when heated with oxygen. It inflames spontaneously in chlorine. Its smell is less disagreeable than that of the former gas. Both of these gases frequently contain free hydrogen, the relative proportion of which may be ascertained by agitation with a cold saturated solution of sulphate of copper, which absorbs the phosphuretted hydrogen, and leaves the pure hydrogen.

Dumas infers from the action of perchloride of mercury on this gas, that 100 measures yield 150 of hydrogen. Dr. Turner, on the authority of Dumas and of Buff (*Ann. Ch. et Ph.*, xli.), considers 100 measures of this variety of phosphuretted hydrogen as constituted of 150 of hydrogen gas, and 25 of the vapor of phosphorus (*Elem. Chem.*), hence if

150 cubic inches of hydrogen weigh	Grains.
25 ,, phosphorus vapor	3·1977
100 ,, phosphuretted hydrogen gas should weigh	33·5425
	36·7402

The calculated density of a gas so constituted should be 1·1853; or, according to Gmelin,

	Vol.	Sp. Gr.	Vols.	Sp. Gr.
Vapor of phosphorus.....	1	4·354	$\frac{1}{4}$	1·088
Hydrogen	6	0·415	$1\frac{1}{2}$	0·104
	4	4·769	1	1·192

And assuming the two gases to be identical in composition, they will contain

				H. Rose.	Dumas.	Leverrier.
Phosphorus	1	32	91·43	91·32	91·51	91·36
Hydrogen	3	3	8·57	8·68	8·49	8·64
Phosphuretted hydrogen gas	1	35	100·00	100·00	100·00	100·00

It has been suspected that the spontaneously inflammable phosphuretted hydrogen derives its peculiarities from the presence of something extraneous, or, according to Leverrier (*Ann. Ch. et Ph.*, lx. 174), to a gaseous compound of phosphorus and hydrogen, PH_2 , which is spontaneously inflammable and decomposed by light. Graham ascertained that Davy's hydrophosphoric gas was not rendered spontaneously inflammable by the presence of phosphorus vapor, and that the spontaneously

inflammable gas was deprived of that property by very minute portions of certain combustible bodies, such as potassium, and the vapor of ether and essential oils; and lastly, that the property was communicated to either gas by the addition of a very minute quantity of nitrous acid vapor, varying from 1-1000th to 1-10,000th of the volume of the gas. (*Phil. Mag.*, v. 401, 3 Ser.) Phosphuretted hydrogen combines with several of the perchlorides, and with the perchloride of tin it forms a compound which is decomposed with the escape of a non-inflammable gas by water, but of a spontaneously inflammable gas by solution of ammonia.

Grotthus has described a liquid compound of phosphorus and hydrogen, analogous probably to the corresponding combination of sulphur, (and, if so, *biphosphuret of hydrogen*,) obtained by boiling phosphorus in an alcoholic solution of potassa. The phosphorus liquifies and remains fluid when cold; if boiled in water, phosphuretted hydrogen is evolved, but no phosphoric acid is formed, nor is the water decomposed; and phosphorus, which concretes as usual, remains behind. According to Magnus, when phosphuret of potassium is thrown into water, a compound of phosphorus and hydrogen precipitates in the form of a yellow powder. These phosphurets of hydrogen have been more lately examined by P. Thenard (*Ann. Ch. et Ph.*, Mai, 1845), whose researches have also explained much that was obscure respecting the varieties of phosphuretted hydrogen and the action of phosphuret of calcium on water. (See *Phosphuret of Calcium*.)

Common phosphorus always yields a trace of hydrogen or of phosphuretted hydrogen, which it evolves when in the act of combining with some of the metals, and Davy found that by acting on fused phosphorus by the voltaic spark, small portions of hydrogen were given off.

HYDRIODATE OF PHOSPHURETTED HYDROGEN. The dry gases condense on mixture into colorless crystals. (LABILLARDIERE, *Ann. Ch. et Ph.*, vi. 304.) When iodine and phosphorus in equal atomic quantities are added to a little water, hydriodic gas is evolved and crystals similar to the above sublime. Probably hypophosphorous acid is first formed which is resolved by the remaining water into phosphoric acid and phosphuretted hydrogen. $2P + 2I + 5HO = PO_5 + PH_3, HI + HI$. (L. GMELIN.) The compound forms brilliant prismatic volatile and deliquescent crystals, which are resolved by water into their component gases: they consist of

	H. Rose.				
Phosphuretted hydrogen	1	...	35	...	21.6 20.91
Hydriodic acid.....	1	...	127	...	78.4 79.09
<hr/>					
Hydriodate of phosphuretted hydrogen.....	1		162		100.0 100.00

PHOSPHORUS AND NITROGEN; PHOSPHURET OF NITROGEN: (see *action of ammonia on chloride of phosphorus*, p. 428.)

AMMONIURET OF PHOSPHORUS. According to Berzelius, when phosphorus is exposed to ammonia standing over mercury, a *phosphuret of ammonia* is produced, of a dark color, and pulverulent texture: its properties have not been examined. Bineau could not succeed in obtaining this compound. (*Ann. Ch. et Ph.*, Lxvii. 229.)

PHOSPHORUS AND SULPHUR; PHOSPHURET OF SULPHUR; SULPHURET OF PHOSPHORUS. These substances may be united by fusion in an exhausted flask, or under water; in the latter case they combine gradually as soon as the phosphorus is melted, but the heat must be cautiously applied, as the water is sometimes suddenly decomposed with explosive violence. Faraday (*Quar. Journ.*, iv. 361) melted 5 parts of sulphur with 7 of phosphorus and agitated the compound in liquid ammonia, by which the reddish-brown color was removed and a pure fluid of a light yellow color, and semi-transparent, remained. It retained its fluidity when cooled down to 20° , and was perfectly liquid at 32° . On remaining for some weeks in a bottle of water it deposited crystals of sulphur, and at the temperature of 40° became a crystalline mass, in which the relative weight of the phosphorus to the sulphur appeared to be as 2 to 1.

Phosphorus	1	32	66·7
Sulphur	1	16	33·3
<hr/>					
Phosphuret of sulphur	1		48		100·0

This purified compound did not act upon water at common temperatures, nor rapidly even at its boiling-point; hence, Faraday infers that the rapid action of the compound formed by heat in a tube when in contact with water, results from some combination of oxygen and phosphorus.

When the liquid terchloride of phosphorus is acted on by sulphuretted hydrogen, hydrochloric acid is evolved, and a yellow substance produced which is a tersulphuret of phosphorus. $3\text{HS} + \text{PCl}_3 = 3\text{HCl} + \text{PS}_3$. (SERULLAS.)

§ X. SELENIUM. Se. 40.

THIS rare substance was discovered in 1817 by Berzelius, during an examination of certain substances found in the sulphuric acid manufactured at Gripsholm, in Sweden. (*Ann. Ch. et Ph.*, ix. 160.) The sulphur used in these works is procured from the iron pyrites of Fahlun, and the acid obtained from it deposits a red matter, which was supposed to contain tellurium, but the peculiarities of which were traced to a distinct and previously unknown substance, to which its discoverer gave the name of *Selenium*, from $\Sigma\epsilon\lambda\eta\nu\eta$, the moon.

Some difference of opinion exists as to the place which selenium should occupy in chemical arrangements. Berzelius includes it among the metals; but as it is a non-conductor of electricity, and a most imperfect conductor of heat, and as, in other respects, it bears much analogy to sulphur, it is generally placed among the non-metallic combustibles.

Stromeyer and Rose have detected it in several metallic ores from the Hartz mines, and amongst some of the volcanic products of the Lipari islands; and it exists in some of the sulphurets of lead of Fahlun, and in the pyrites of the isle of Anglesey.

Selenium is most readily obtained by the decomposition of *selenic acid*, which may be effected by adding hydrochloric acid to its solution in water, and immersing a plate of zinc in the mixture: a gray or reddish-brown flocculent precipitate of selenium is then deposited. Berzelius, in his *Lehrbuch der Chemie*, has detailed the circuitous process by which he

separated selenium from the red sediment of the Gripsholm sulphuric acid (see also *Ann. of Phil.*, xiii., 401, and *Ann. Ch. et Ph.*, ix. 160). Lewenau has described some important improvements in the modes of obtaining it in a pure state. (*Ann. of Phil.*, N.S., viii. 104.)

To extract selenium from the native sulphuret, Magnus proposes to mix it with eight times its weight of peroxide of manganese, and to expose the mixture to a low red heat in a glass retort, the beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid, while the selenium either sublimes as such or in the state of selenious acid: should any of the latter go over into the water it would there be reduced by the sulphurous acid. (TURNER, *Elem. of Chem.*)

Selenium, when cooled after fusion, has a reddish-brown color, and dim metallic lustre; its fracture is of a lead-gray color. Its specific gravity is 4.32. Specific heat = 0.0837. (REGNAULT.) Obtained from its solutions by precipitation upon zinc, it is red, but becomes black when boiled in water. A dilute solution of selenic acid mixed with sulphurous acid, and exposed to light, becomes covered with a film of reduced selenium of a gold color. When fused, and very slowly cooled, its surface is gray and granular, without lustre: and its fracture dull, like that of metallic cobalt. It is brittle, soft, and easily reduced to powder, is a non-conductor of electricity, but not idioelectric. (BERZELIUS.) Knox found it to transmit electricity when in fusion, from a battery of 60 pairs; and Bonsdorf rendered it electric by friction, when perfectly dry. Under certain circumstances, it assumes a prismatic crystalline texture, but not very distinct: in thin layers it is transparent, transmitting red rays: it is softened by heat, becoming semifluid at 212° , and perfectly fusing at a temperature somewhat higher; it remains for some time soft on cooling, and may be drawn out into filaments like sealing-wax, which are of a gray metallic lustre by reflected light, but by transmitted light of a clear ruby-red. Heated in a tube or small retort nearly to redness, or about 650° , it boils, and is converted into a yellow vapor of a deeper color than chlorine, which condenses into black drops that run together like quick-silver. Heated in the open air it rises in vapor, which may be condensed into a red powder. It is characterized by tinging the flame of the blow-pipe of a light blue color, and by exhaling, when strongly heated, a peculiar and highly diffusible odor of decayed horseradish. Assuming the combining volume of selenium vapor to be the same as that of sulphur vapor, and that 1 volume of selenious acid includes 1 volume of oxygen, and one-sixth of a volume of selenium vapor, the density of the latter would by calculation be 16.6392 (air = 1), and 100 cubic inches would weigh 515.8 grs. Its density compared with hydrogen would be 240.

SELENIUM AND OXYGEN. These bodies appear to unite in three proportions, forming an oxide and two acids.

SELENIOUS OXIDE; OXIDE OF SELENIUM, SeO_2 , is formed by heating selenium in a limited quantity of atmospheric air, and washing the product to separate a portion of acid which is at the same time formed. The characters of this compound have not been accurately examined, nor has its composition been ascertained; it is sparingly soluble in water, and

passed through alkaline solutions, imparts to them its peculiar odor, but is not absorbed; it does not redden litmus. It appears to be the cause of the peculiar odor emitted during the oxidation of selenium. It probably consists of

Selenium	1	40	88.3
Oxygen	1	8	16.7
	<hr/>		<hr/>		<hr/>
	1		48		100.0

SELENIOUS ACID. SeO_2 . When a current of oxygen gas is passed over selenium, heated to its boiling-point, it burns with a pale bluish-green flame, and this acid sublimes and condenses in long brilliant prismatic crystals, provided the vessel into which it is received is cold and capacious; otherwise, the sublimate is semifused and semitransparent: this is dry selenious acid: it loses its transparency by exposure to air, and rapidly absorbs water; its vapor is of the color of chlorine. Selenious acid may also be obtained by digesting selenium in nitric or nitrohydrochloric acid till entirely dissolved, and then evaporating to dryness. Its taste is sour and hot: its odor, when sublimed, acrid, but not like that of the oxide. It is very soluble in warm water, and the solution furnishes crystals of hydrated acid, which when heated, part with their water before the acid itself rises in vapor. It also dissolves in alcohol, and the solution furnishes, on distillation, a liquid of an ethereal odor. If this alcoholic solution be mixed with sulphuric acid, and then distilled, the product has an odor so insupportable, that Berzelius was unable to proceed in its examination.

The selenious acid and its salts may be decomposed by mixture with solution of sulphite of ammonia and the addition of hydrochloric acid. The selenium is slowly reduced, the solution first acquiring a yellow color, and in the course of some hours depositing red flocculi of selenium: $\text{SeO}_2 + 2\text{SO}_2 = \text{Se} + 2\text{SO}_3$: the effect is accelerated by a boiling heat, and by exposure to sunshine. This acid forms precipitates in the solutions of silver and of lead; its neutral salts with alkaline bases convert vegetable blues to green, and redden turmeric: with sulphuretted hydrogen it forms sulphuret of selenium and water: $\text{SeO}_2 + 2\text{HS} = \text{SeS}_2 + 2\text{HO}$.

The proportion of oxygen in this acid is, to that contained in the bases to which it unites to form neutral salts, as 2 to 1; so that it may be considered as a compound of

Berzelius.					Vols.	Sp.Gr.	Vols.	Sp.Gr.											
Selenium	1	...	40	...	71·4	...	71·21	Selenium vapor	1	...	16·64	...	$\frac{1}{6}$...	2·773				
Oxygen	2	...	16	...	28·6	...	28·79	Oxygen gas.....	6	...	6·65	...	1	...	1·109				
<hr/>					<hr/>					<hr/>					<hr/>				
Selenious acid	1		56		100·0		100·00	Vapor	6		23·29		1		3·882				

SELENITES. The selenious acid combines in 1, 2, and 4 equivalents with bases: it forms few subsalts. The neutral salts (MO, SeO_2) are alkaline, and the bisalts ($\text{MO}, 2\text{SeO}$) acid to test paper: the quadrisalts are limited to the alkalis. Heated with sal ammoniac these salts yield a sublimate of selenium. The neutral selenites of ammonia, potassa, and soda are soluble in water; the other salts difficultly, or insoluble: the supersalts are soluble. All the selenites are soluble in nitric acid, and in alcohol. (BERZELIUS.)

SELENITE OF AMMONIA. Selenious acid, dissolved in slight excess of strong water of ammonia, and left to evaporate in a warm place, yields four-sided prisms and plates, and deliquescent plumose crystals: when heated, a portion of quadriselenite of ammonia sublimes and fused selenium remains. Their solution, exposed to air, loses ammonia and deposits acicular crystals of *biselenite*. The *quadriselenite* is deliquescent and uncrystallisable. (BERZELIUS.)

SELENIC ACID. SeO_3 . This acid was first described by Mitscherlich and Nitzsch. (*Ann. Ch. et Ph.*, xxxvi. 100.) It is obtained by fusing selenium, or selenious acid, or any of its salts, or a metallic seleniuret, with nitrate of potassa or of soda: seleniuret of lead, as the most common ore containing it, has generally been used: it is to be digested in hydrochloric acid, to separate carbonates, and the residue mixed with its weight of nitrate of soda, and gradually thrown into a red-hot crucible; the fused mass is then well washed in hot water, which dissolves the alkaline seleniate and the nitrate: this solution, quickly boiled down, deposits seleniate of soda, and this being separated, the nitrate crystallizes on cooling: the mother-liquor again boiled deposits more of the seleniate, and in this way the salts may be separated; for the seleniate, like sulphate of soda, is more soluble in water at about 90° than at 212° . The seleniate of soda thus obtained is not quite pure; if it be mixed with hydrochlorate of ammonia and heated, nitrogen and water are evolved, selenium sublimes, and chloride of sodium is formed: the selenium is now pure, and may be converted by nitric or nitrohydrochloric acid into selenious acid, neutralized with soda, and this converted into seleniate by fusion with nitrate of soda, solution, and crystallization, as before. The solution of this pure seleniate may now be decomposed by nitrate of lead; the insoluble seleniate of lead is well washed and diffused through water, into which a current of sulphuretted hydrogen is passed to precipitate the lead; the liquid is boiled, to evaporate excess of sulphuretted hydrogen, and is now dilute selenic acid, and may be concentrated by careful evaporation. Its purity, as respects fixed bodies, is determined by its perfect volatility; if sulphuric acid be present, it may be ascertained by boiling a portion with hydrochloric acid, which produces selenious acid, and then testing by chloride of barium.

Selenic acid is a colorless liquid, which may be heated to about 536° without decomposition; it is partially changed at higher temperatures; and at 554° , is rapidly resolved into selenious acid and oxygen. When concentrated, by exposure to a temperature of about 329° , it acquires a specific gravity of 2.524; at 513° , it is 2.6: it may be rendered somewhat denser by evaporation at higher temperatures; but in that case a portion of selenious acid is formed in it; and it is impossible to expel the whole of its water without decomposition: it is unknown in its anhydrous state. The hydrated acid may be represented by HO,SeO_3 , or H,SeO_4 .

Selenic acid has a strong attraction for water, and evolves much heat when mixed with it; sulphuretted hydrogen does not decompose it, and hence that gas may be used to decompose some of the metallic seleniates. When boiled with hydrochloric acid, selenious acid and chlorine are produced, so that the selenio-hydrochloric acid dissolves gold upon the same principle as the nitro-hydrochloric. It dissolves zinc and iron

with the evolution of hydrogen; and copper, with the production of selenious acid; sulphurous acid, which decomposes selenious acid, has no action on selenic acid; so that to decompose selenic acid in this way, it must first be boiled with hydrochloric acid, which converts it into selenious acid, and the sulphurous acid, or a sulphite, then effects the separation of selenium. The affinity of selenic acid for bases is little inferior to sulphuric acid, for seleniate of baryta is not completely decomposed by sulphuric acid.

From the resemblance, in crystalline form, of the seleniates to the sulphates, Mitscherlich inferred that the proportion of oxygen in selenic acid should correspond to that in sulphuric acid; that it should be to the base as 3 to 1; and to that in the selenious acid as 3 to 2. These views were confirmed by experiment; the selenic acid, therefore, consists of

						Mitscherlich.
Selenium	1	40	62·5 61·4
Oxygen	3	24	37·5 38·6
<hr/>						<hr/>
Selenic acid	1		64		100·0	100·0

SELENIATES. The selenic and sulphuric acids are isomorphous, as are the seleniates and sulphates (also the chromates and manganates). The seleniates mostly withstand a red-heat: they are more easily reduced at high temperatures by hydrogen, than the sulphates. Heated with sal ammoniac, they are decomposed with the separation of selenium. The seleniates of baryta, strontia, lime, and lead, are almost insoluble in water and in dilute nitric acid. (MITSCHERLICH.)

SELENIUM AND CHLORINE. When chlorine is passed over selenium, it is absorbed with the production of heat, and a brown liquid results, not very volatile, and heavier than water. It contains, according to Berzelius, 2 atoms of selenium and 1 of chlorine, and is gradually resolved by the action of water into selenium and hydrochloric and selenious acids. $2\text{Se}_2, \text{Cl} + 2\text{HO} = 3\text{Se} + 2\text{HCl} + \text{SeO}_2$.

Exposed to excess of chlorine, it absorbs an additional quantity, and becomes converted into a white solid *bichloride* $= \text{SeCl}_2$, which volatilizes when heated, and condenses in the form of delicate crystals. It dissolves with the evolution of heat in water, producing a solution of hydrochloric and selenious acids. $\text{SeCl}_2 + 2\text{HO} = \text{SeO}_2 + 2\text{HCl}$. H. Rose has described a compound of chloride of selenium and anhydrous sulphuric acid (*Poggend.* xlv. 315) $= 2 [\text{Se}_2\text{Cl}_5] + 5\text{SO}_3$? (L. GMELIN.)

SELENIUM AND BROMINE. These substances readily combine with the evolution of heat into a reddish-brown fuming compound, having the odor of chloride of sulphur; it is converted by the action of water into hydrobromic and selenious acids. (SERULLAS, *Ann. Ch. et Ph.*, xxxv. 349.)

SELENIUM AND IODINE in equivalent proportions fuse together into a dark-gray mass, from which alcohol abstracts iodine. (TROMSDORFF, *Journ. der Pharm.*)

SELENIUM AND FLUORINE. When selenium vapor is passed over fluoride of lead fused in a platinum vessel, volatile crystals of fluoride of selenium are obtained, decomposed by water, but soluble in hydrofluoric acid. (G. J. KNOX.)

SELENIUM AND HYDROGEN; SELENIURETTED HYDROGEN; HYDROSELENIC ACID. HSe . This gaseous compound may be obtained by the action of hydrochloric acid upon seleniuret of potassium or of iron. It is colorless, and readily dissolves in water, forming a solution at first colorless, but after a time acquiring a reddish hue; the solution smells and tastes somewhat like that of sulphuretted hydrogen; it reddens litmus, and permanently tinges the skin of a reddish-brown. Nitric acid dropped into it occasions no change, and the gas does not readily escape from the water; but, when exposed to air, the solution gradually reddens, and deposits selenium. It occasions precipitates in all solutions of neutral metallic salts, which are black or dark-brown, with the exception of those from zinc, manganese, and cerium, which are flesh-colored. (BERZELIUS.) Bineau observes, that when collected over impure mercury, it is gradually resolved into hydrogen gas. Heated with tin, 1 volume yields 1 volume of hydrogen and seleniuret of tin. (*Ann. Ch. et Ph.*, LXVII. and LXVIII.)

Seleniuretted hydrogen is decomposed by the joint action of air and water; it is absorbed by moist substances, and soon communicates to them a red color. The selenium is thus remarkably deposited throughout the texture of organic bodies. A piece of moist paper is penetrated by the red color. Moist wood, and even a thin piece of caoutchouc, became in the same way red throughout. It exerts a dangerous action upon the trachea and organs of respiration; it inflames the eyes, and painfully stimulates the nasal membrane, destroying for some hours the sense of smell. Berzelius states that in the first experiment which he made upon this gas, he let up into his nostrils a bubble about the size of a pea. "It deprived me so completely of the sense of smell, that I could apply a bottle of concentrated ammonia to my nose without perceiving any odor. After five or six hours I began to recover the sense of smell, but a severe catarrh remained for about fifteen days." On another occasion, a little of the gas accidentally escaped; it produced a sharp sensation in the nose, red eyes, and a dry and painful cough, at length succeeded by expectoration tasting like the vapor from a boiling solution of corrosive sublimate. "These symptoms were removed by a blister to my chest. The quantity of seleniuretted hydrogen gas which on each of those occasions entered into my organs of respiration, was much smaller than would have been required of any other inorganic substance whatever to produce similar effects." (*Ann. of Phil.*, xiv. 101.) Dr. Prout, in his *Bridgewater Treatise*, quotes the above passage, to show how small a quantity of foreign matter may, when diffused in the atmosphere, produce powerful effects upon the human system, and suggests the possibility of some such cause as the origin of influenza, and some other epidemic disorders.

The specific gravity of seleniuretted hydrogen has not been experimentally ascertained, but from its analysis (BERZELIUS, *Ann. Ch. et Ph.*, ix. 335), it appears to consist of

Berzelius.								Vols.	Sp. gr.	Vols.	Sp. gr.				
Selenium	1	...	40	...	97.56	...	97.4	Selenium vapor	1	...	16.64	...	$\frac{1}{6}$...	2.773
Hydrogen.....	1	...	1	...	2.44	...	2.6	Hydrogen gas	6	...	0.41	...	1	...	0.069
<hr/>															
Seleniuretted } hydrogen.... }	1		41		100.00		100.0	Seleniuretted } hydrogen gas }	6		17.05		1		2.842

HYDROSELENIATE OF AMMONIA. SELENIURET OF AMMONIUM. NH_3 , HSe , or Se, NH_4 . 1 volume of seleniuretted hydrogen gas condenses 2 volumes of ammonia, forming a white uncrystallizable deposit, giving a reddish solution with water. Equal volumes of the gases $= \text{NH}_3, 2\text{HSe}$, yield a white crystalline compound: they are decomposed by exposure to air with the separation of selenium. (BINEAU, *Ann. Ch. et Ph.*, LXVII. 229.)

SELENIUM AND NITROGEN have no mutual action, nor does selenium absorb ammonia; but when seleniuret of calcium and hydrochlorate of ammonia are mixed and distilled, a red fluid is obtained, of an hepatic odor, and decomposed by exposure to air, exhaling ammonia, and leaving selenium.

SELENIUM AND SULPHUR. Sulphur and selenium may be mixed by fusion in all proportions. An addition of about one per cent. only of sulphur renders selenium more red, fusible, and transparent when cold. *Bisulphuret of selenium*, SeS_2 , may be obtained by passing sulphuretted hydrogen into a solution of selenious acid: the fluid becomes turbid, and acquires a fine yellow color, but the precipitate is long in separating, unless a little hydrochloric acid be added: when warmed, it acquires a red color and viscid texture, and may be distilled, without decomposition, at high temperatures. It is slowly acted upon by nitric acid, but nitrohydrochloric acid easily decomposes it; it is soluble in the caustic fixed alkalis, and in their hydrosulphurets, forming yellow solutions, from which acids precipitate it. Burned in the air, it at first exhales a sulphurous odor, but afterwards the smell of horseradish prevails. It consists of

						Berzelius.
Selenium	1	40	55.6 55.21
Sulphur.....	2	32	44.4 44.79
<hr/>						<hr/>
Bisulphuret of selenium	1		72		100.0	100.00

SELENIUM AND PHOSPHORUS; PHOSPHURET OF SELENIUM. Dropped into melted phosphorus, selenium forms a red compound, apparently soluble in all proportions in the fused phosphorus. When phosphorus is saturated with selenium, an easily-fusible compound results, which, on cooling, acquires a brown lustre and vitreous fracture. When this *phosphuret of selenium* is digested in water, a small portion of the phosphorus is oxidized, and the water acquires the odor of seleniuretted hydrogen, and deposits selenium when exposed to the air. The compound is dissolved when boiled in caustic potassa, and the solution contains phosphate and hydroseleniuret of potassa. (BERZELIUS, *Ann. Ch. et Ph.*, ix. 238.)

§ XI. CARBON. C. 6.

THE purest form of this important and abundant element, is the *diamond*, a mineral first discovered in Asia, in the provinces of Golconda and Visapour, in Bengal, and in the island of Borneo. About the year 1720, diamonds were found in the district of Serra Dofrio, in Brazil, and from this locality the European market is now chiefly supplied. The Brazilian mines are stated to furnish from 10 to 13 lbs. weight of diamonds annually: of which not more than from 800 to 900 carats are fit for jewellery,

the rest, under the name of *Bort*, being used for other purposes. But if the diamonds fit for cutting are few, those which are tolerably large, pure in color, and free from defects, are still more rare. All the largest diamonds are from Golconda: the largest Brazilian diamond on record is in possession of the crown of Portugal, but it has not been cut or polished: it weighs 95 carats. Diamonds occur in detached crystals in alluvial soil; though it appears probable, from a specimen described by Mr. Heuland (*Geol. Trans.*, 2nd Series, i. 419), that in Brazil the real matrix is an iron-stone which forms beds resting on primary chlorite slate. According to Mr. Voysey, the diamonds of the Nalla Malla Mountains, in Hindostan, are found in a species of pudding-stone or breccia, composed of fragments of jasper, quartz, and calcedony. (*Phil. Mag.*, 2nd Series, i. 147.) The primitive form of the diamond is the regular octohedron, each triangular facet of which is sometimes replaced by six secondary triangles, bounded by curved lines; so that the crystal becomes spheroidal, and presents forty-eight facets. Diamonds, with twelve and twenty-four facets, are not uncommon. (JAMESON'S *Mineralogy*, 2nd edit., vol. i. p. 1.) The diamond has been found nearly of all colours: those which are colorless are most esteemed; then those of a decided red, blue, or green tint. Black diamonds are extremely rare. Those which are slightly brown, or tinged only with other colors, are least valuable.

The fracture of the diamond is foliated, its laminae being parallel to the sides of a regular octohedron. It is somewhat brittle but very hard; its specific gravity varies from 3·4 to 3·6, it is most commonly 3·52. It is a non-conductor of electricity, frequently phosphorescent (p. 120), and has a very high refractive and dispersive power in regard to light, as compared with its density (p. 91). It is not acted upon by any solvent. It is combustible, and burns in the air at high temperatures, into carbonic acid. All attempts to fuse or crystallize carbon, in other words to form diamonds artificially, have signally failed. Some suppose the carbon of the diamond to be of organic origin, and from traces of silica and iron contained in the residue of their combustion, and the careful microscopical examination of their ash, Petzold has inferred traces of vegetable parenchyma (*Journ. für praktisch. Chem.*, xxiii. 475.) Göbel supposes the carbon derived from carbonate of lime, and reduced at high temperatures by the metals of the earths, (*Poggend.*, xx. 539;) these opinions, however, are not supported, and we can only surmise either that the diamond is derived from carbon which has been slowly cooled from the state of fusion, or that it has crystallized from some unknown solvent: for there are many diamonds which, when burned, leave no residue, though from others it may amount to as much as 0·15 or even 0·2 per cent., being partly a brownish powder, and partly yellowish crystalline particles. (DUMAS and STAS, *Ann. Ch. et Ph.*, LXXvi. 1; ERDMANN and MARCHAND, *Journ. für pr. Chem.*, xxiii. 159.)

The art of cutting and polishing diamonds, though probably of remote antiquity in Asia, was first introduced into Europe in 1456, by Louis Berghen, of Bruges, who accidentally discovered, that, by rubbing two diamonds together, a new facet was produced. The particular process of forming the rough gems into *brilliants* and *rose diamonds* has been described at length by Jeffries. (*On Diamonds and Pearls*, 3rd edit., London, 1800.) By either of these processes, but especially by the for-

mer, so much is cut away, that the weight of the polished gem does not exceed half that of the rough stone; so that the value of a brilliant-cut diamond is esteemed equal to that of a similar rough diamond of twice the weight, exclusive of the cost of workmanship. The weight, and therefore the value of diamonds, is estimated in *carats*, 150 of which are about equal to one ounce troy, or 480 grains. They are divided into halves, quarters, or carat grains, eighth, sixteenth, and thirty-second parts.

The difference of value between one diamond and another of equal merit, is, generally speaking, as the squares of their respective weights: thus, the value of three diamonds, of one, two, and three carats' weight respectively, is as one, four, and nine. The average price of rough diamonds is estimated by Jeffries at 2*l.* per carat; and, consequently, when wrought, the cost of the first carat, exclusive of workmanship, will be 8*l.*, which is the value of a rough diamond of two carats.

				£.
A wrought diamond of 3 carats is worth				72
„	4 ditto	„	126
„	5 ditto	„	200
„	10 ditto	„	800
„	20 ditto	„	3,200
„	30 ditto	„	7,200
„	40 ditto	„	12,800
„	50 ditto	„	20,000
„	60 ditto	„	28,800
„	100 ditto	„	80,000

This mode of valuation, however, only applies to small diamonds, in consequence of the difficulty of finding purchasers for the larger ones.

The largest known diamond is probably that mentioned by Tavernier, in the possession of the Great Mogul: its size is about that of half a hen's egg: it is cut in the rose form, and when rough, is said to have weighed 900 carats: it was found in Golconda about the year 1550. Among the crown-jewels of Russia is a diamond weighing 195 carats: it is the size of a small pigeon's egg, and was formerly the eye of a Brahminical idol, whence it was purloined by a French soldier; it passed through several hands, and was ultimately purchased by the Empress Catherine, for the sum of 90,000*l.* in ready money, and an annuity of 4000*l.* Perhaps the most perfect and beautiful diamond hitherto found, is a brilliant brought from India by an English gentleman of the name of Pitt, who sold it to the Regent Duke of Orléans, by whom it was placed among the crown jewels of France: it weighs rather more than 136 carats, and was purchased for 100,000*l.* In the year 1828, a collection of diamonds of extraordinary size and beauty was in the possession of Messrs. Rundell, Bridge, and Co., of London: the suite consisted of eight, of various shapes and sizes, the smallest weighing 55 grains, and the largest 151 grains: with one exception they were all brilliant cut.

The principal use of the diamond is in ornamental jewellery, but it is also importantly applicable in some of the arts; in consequence of its extreme hardness it is employed for the pivot-holes in delicate watch and clock work, and it has been used to form the holes through which extremely fine wires are drawn: it also furnishes the only convenient tool for cutting glass; for this purpose the edge of one of the small curvilinear crystals is used, for the edges of the crystals formed by flat plates only scratch, without producing that peculiar fissure by which the glass

can be smoothly split. (WOLLASTON, *Phil. Trans.*, 1816, p. 265.) Microscopic lenses have also been formed of diamond.

CHARCOAL. This is another well-known form of *carbon*: it is obtained in abundance by the destructive distillation of various organic products, and its characters and properties vary with its source. It may be prepared by heating pieces of wood in a close vessel, or in a crucible covered with sand, to redness, and keeping them in that state for about an hour, or till all volatile matters are expelled. They are thus converted into a black brittle porous substance, which appears to be essentially the same, from whatever kind of wood it has been procured. Sugar and certain other substances which neither contain nitrogen nor leave any residue after combustion, when intensely heated in closed vessels yield a very pure charcoal; it always, however, retains traces of oxygen and hydrogen; thus, Erdmann and Marchand found in the carbon of sugar obtained at a white heat, 3.1 per cent. of oxygen, and 0.6 of hydrogen: even after it had been subjected for 3 hours to the highest temperature of a blast-furnace, it retained 0.5 per cent. oxygen, and 0.2 hydrogen. By passing the vapors of certain hydrocarbons, and of oils, alcohol, and ether, through white-hot porcelain tubes, very pure forms of carbon are also deposited.

Common charcoal, employed as fuel, is usually made of oak, chestnut, elm, beech, or ash wood, the resinous woods being seldom used. Young wood affords a better charcoal than large timber, which is also too valuable to be thus employed. The billets are formed into a conical pile, which, being covered with earth or clay, is suffered to burn with a limited access of atmospheric air, by which its complete combustion, or reduction to ashes, is prevented. (See URE's *Dict. of Arts*, Art. *Charcoal*.)

Another, and a more perfect mode of preparing charcoal, consists in submitting the wood to a red heat in a kind of distillatory apparatus consisting of cast-iron cylinders, from which issue one or more tubes for the escape of gaseous matters and vapors. The makers of gunpowder particularly prefer this process. (A plate of this apparatus is given in PARKES' *Chemical Essays*.)

The quantity of charcoal obtained from different kinds of wood is liable to much variation. The following table drawn up from the experiments of Allen and Pepys (*Phil. Trans.*, 1807), and of Griffiths, (*Quar. Jour.*, xvi. 264), shows the produce of charcoal from 1000 parts of several varieties of dense and light woods.

Ebony.....	305	Box.....	202
Botany Bay-wood	281	Fir	181
Brazil-wood	260	Lignum-vitæ	175
Eveoas-wood	225	Oak.....	174
King-wood.....	220	Mahogany	157
Tulip-wood.....	208	Beech.....	150
Satin-wood.....	207		

Charcoal is a black, insoluble, inodorous, insipid, brittle substance. According to J. Davy, charcoal in extremely thin filaments is translucent: he found the light transmitted to vary in its hues from almost white, as in the instance of the thinnest plates of the charcoal of the pith of elder, to brown and red of various shades, in the instances of lamp-

black, anthracite, and plumbago. (*Ed. Phil. Trans.*) It is an excellent conductor of electricity, but a bad conductor of heat; unchanged by the combined action of air and moisture at common temperatures, and easily combustible in oxygen gas. Its specific heat, as estimated by Regnault, is 0.24111; the average, as given by Dulong and Petit, is 0.25. When pure it is perfectly infusible at all known temperatures; in the cases in which it was supposed to have been fused, some impurities apparently have existed in the charcoal employed; upon this subject a series of experiments have been published by Silliman. (*Quarterly Journ.*, xvi. 157.) Under common circumstances of ignition it does not appear to volatilize, but from the experiments of Leplay and Laurent (*Ann. Ch. et Ph.*, lxxv. 417), it seems not improbable that in the process of steel-making the penetration of iron by carbon may be partly due to its volatility; and in the voltaic ignition of charcoal points, carbon passes from the positive to the negative side in the arc of flame: so that a concavity ensues upon the surface whence the + electricity emanates, and concretion upon the opposite pole. It is capable of destroying the smell and taste of a variety of vegetable and animal substances, and of abstracting certain substances dissolved in fluids. (Lowitz, *Crell's Annals*, ii. 165.) The use of charring piles; of throwing charcoal into putrid water; of wrapping it in clothes that have acquired a bad smell; of adding it to port wine, with a view of making it tawny, depends upon the above properties; but its most important application of this kind, is in the sugar refinery. M. Bussy has published some interesting observations on the discoloring power of charcoal, in the *Journal de Pharmacie* for June, 1822, of which an abstract will be found in the *Quarterly Journal*, xiii. 406. It appears from his experiments, that certain physical conditions are requisite for the manifestation of this property, especially porosity, minute division, and a dull earthy aspect; and that it is not possessed by any hard and brilliant charcoal even when finely powdered. Upon this principle, he accounts for the superior efficacy of certain charcoals obtained by burning animal substances, over that of vegetables, in the destruction of color. According to Payen, animal charcoal, boiled with lime-water, deprives it entirely of lime, an effect not produced by lamp-black or vegetable charcoal. (*Quarterly Journal*, xv. 384.) Well-burned charcoal shaken with water contaminated by sulphuretted hydrogen, entirely deprives it of that gas, so that when filtered it is not only inodorous, but is not discolored by solution of lead. Warrington has observed that the salts of the vegetable alkaloids, such as sulphate of quinia, &c., are abstracted from their solutions by animal charcoal, and has mentioned several inorganic salts which are similarly removed. (*Mem. Ch. Soc.*, 1845.) He was led to this inquiry by attempting to decolor ale, so as to give it the pale tint prized in the India market, when the whole of the bitterness was found to be abstracted by filtration through animal charcoal. Hopff (*Journ. de Pharm.*, xvii. 172), and Chevallier, (*The Chemist*, April, 1844), have also experimented upon this subject. These peculiar powers of charcoal in abstracting not merely coloring and odorous matters, but also other organic and inorganic bodies from their solutions, should render chemists extremely cautious in resorting to it in analytical inquiries.

When animal charcoal which has been used for the purpose of de-

coloration is again burned, it regains its former efficacy, provided its texture is not materially changed; and the bone charcoal (retaining the phosphate of lime) after it has been used by the sugar refiner, is frequently burned and re-employed several times successively; at length, however, from the prevalence of the charcoal derived from the adhering sugar, and the destruction of the original character of the article, its powers become so far diminished as not to be worth reburning.

Newly-made charcoal has the property of absorbing certain quantities of the different gases. Upon this subject the experiments of M. Theodore de Saussure are the most recent. (THOMSON'S *Annals*, vol. vi.) The charcoal was heated red-hot, then suffered to cool under mercury, and introduced into the gas. The following are the volumes of different gases absorbed by a volume of charcoal = 1.

Ammonia	90	Bicarburetted hydrogen	35
Hydrochloric acid	85	Carbonic oxide	9.42
Sulphurous acid	65	Oxygen	9.25
Sulphuretted hydrogen	55	Nitrogen	7.5
Nitrous oxide	40	Carburetted hydrogen.....	5
Carbonic acid	35	Hydrogen	1.75

The absorption was always at its maximum at the end of twenty-four hours, not being increased by retaining the charcoal longer in the gas. When charcoal, already saturated with any one gas, is put into another, it gives out a portion of the gas already absorbed, and takes up a portion of the new gas. It would also appear that this absorptive quality partly depends upon the mechanical texture of the charcoal, and consequently will vary in the different woods; for, by exposing the charcoal of different woods to air, Allen and Pepys found that they increased very differently in weight. By a week's exposure, charcoal from

Lignum-vitæ gained	9.6 per cent.	Beech.....	16.3 per cent.
Fir	13.0 ,,	Oak	16.5 ,,
Box.....	14.0 ,,	Mahogany	18.0 ,,

The matter absorbed in these cases consisted principally of aqueous vapor, which is very greedily imbibed by newly-made charcoal.

According to Vogel, when recently-ignited charcoal, which has been cooled under mercury, is put into a jar of atmospheric air, it absorbs the oxygen of the air to a greater extent than the nitrogen. (SCHWEIGGER'S *Journal*, iv.) A piece of well-burned charcoal cooled under mercury and then introduced into a mixture of oxygen and sulphuretted hydrogen gases rapidly absorbed them, and then became ignited and caused explosion. (A. TAYLOR.)

Wood charcoal generally contains about one-fiftieth of its weight of alkaline and earthy salts, which remain in the form of *ash*, after its combustion, but the quantity and quality of this ash vary considerably in different trees and plants.

Animal charcoal, obtained by the carbonization of animal substances, such as muscle, horn, or hoof, resembles the former in its general characters, but instead of retaining the form of the matter from which it is produced, as is the case with the generality of vegetable charcoal, it appears as if it had undergone fusion, and often has a peculiar lustre and sponginess. In all animal charcoals we discover traces of nitrogen, derived probably from the presence of paracyanogen, or of mellone: they also con-

tain the fixed saline and other bodies which existed in their respective sources. The residuary charcoal, obtained by the distillation of bone, is called *bone-black* and *ivory-black* in commerce, and is mixed with the phosphate of lime and other salts contained in the earthy part of the bone, so that for some purposes it requires to be freed from these salts by digesting it in dilute hydrochloric acid, and then washing and drying it. Some of the peculiarities of animal charcoal as regards the destruction of odors and color have already been mentioned, and have been referred to its peculiar texture, rather than to any peculiarity of composition, charcoal being essentially the same, under all its various forms. When vegetable matters, for instance, mixed with earthy substances are charred, they yield a product the properties of which resemble those of animal charcoal: thus a mixture of 100 parts of thin pipe-clay, 20 of tar, and 500 of powdered coal dried and calcined, gave a charcoal of great decolorizing power. Of the different kinds of charcoal used for decoloration, bone charcoal, or ivory-black, is comparatively feeble, although it is superior to wood charcoal. The following table shows the efficiency of several varieties of these charcoals compared with ivory-black. Column I. represents 1 gramme (or 15·4 grains) of the different kinds of charcoal experimented on. Column II. shows the quantity of test indigo liquor (in grammes) decolored by each gramme of the respective charcoals; this indigo liquor contained one-thousandth of indigo, so that each gramme of the decolored liquor represents a thousandth of a gramme of indigo absorbed by the charcoal. Column III. shows the relative decoloration of a solution of 1 part of raw sugar in 20 of water, also in grammes. Column IV. shows the relative decoloration of the indigo, and Column V. that of the brown syrup, in reference to the effect of ivory-black.

I.	II.	III.	IV.	V.
1. Common bone charcoal, or ivory-black	32	9	1·00	1·00
2. Oil charred with phosphate of lime.....	64	17	2·00	1·90
3. Bone charcoal washed with hydrochloric acid	60	15	1·87	1·60
4. No. 3 calcined with carbonate of potassa	1450	180	45·00	20·00
5. Calcined lamp-black	128	30	4·00	3·30
6. No. 5 calcined with carbonate of potassa	550	90	15·20	10·60
7. Charcoal of carbonate of soda decomposed by } phosphorus	380	80	12·00	8·80
8. Charcoal of acetate of potassa.....	180	40	5·60	4·40
9. Starch calcined with carbonate of potassa	340	80	10·60	8·80
10. Albumen or gelatin calcined with carbonate of } potassa	1115	140	35·00	15·50
11. Blood charred with phosphate of lime	380	90	12·00	10·00
12. Blood charred with carbonate of lime	570	100	18·00	11·00
13. Blood charred with carbonate of potassa	1600	180	50·00	20·00

LAMP-BLACK is prepared principally by the combustion of refuse and residuary resin, left by the distillation of turpentine. It is burned in a furnace, so constructed that the dense smoke arising from it may pass into chambers hung with old sacking, where the *soot* is deposited, and from time to time swept off, and sold without any further preparation. (AIKIN'S *Dictionary*, Art. *Charcoal*. DUMAS, *Chim. app. aux Arts*.) When lamp-black has been heated red-hot, it may be regarded as a very pure form of charcoal, for it burns entirely away, and leaves no residuary ash, but, as above observed, it retains traces of oxygen and hydrogen. A substance analogous to lamp-black is obtained by passing the vapor of

certain oils, and of hydrocarbonous compounds, through red-hot tubes; at that high temperature they are more or less perfectly decomposed, and let fall a quantity of very impalpable charcoal, in which, however, as in lamp-black, traces of hydrogen may be detected. One of the principal uses of lamp-black is in the manufacture of printers' ink. For this purpose it has lately been obtained by the combustion of purified coal-tar. (URE'S *Dict. of Arts*, Art. *Black*.) *Spanish-black* is the carbon of cork; *Vine-black*, that resulting from vine-tendrils, and *Peach-black* from peach kernels: the two former have a brownish tint, and the latter a bluish tint. *German* or *Frankfort-black*, is said to be obtained by the carbonisation of a mixture of grape and wine lees, peach kernels, and bone shavings, and to be especially fit for copperplate printing.

COAL-GAS CHARCOAL. A singular form of pure charcoal is occasionally deposited in coal-gas retorts, and in the tubes connected with them, resulting from the decomposition of the first products of the distillation of coal. It has a gray color, and often exhibits a laminated texture; its streak is black, and it breaks with an earthy fracture: its specific gravity is about 1·8. It sometimes happens that the gas escapes through some crack in the retort, in which case a peculiar carbonaceous deposit forms upon the surrounding brick-work, of a stalactitic character, an iron-gray color, and considerable lustre; it does not easily burn, nor does it soil the fingers; and some specimens, from their appearance, might be considered as metallic. Its specific gravity is about 1·75. Some years ago, Mr. Charles Macintosh, of Glasgow, made steel by passing coal-gas over ignited iron placed in an air-tight iron chest: in this process much carbon was deposited in various states, but some of it assumed the remarkable form of capillary filaments, and tufts of a metallic lustre; they were very difficult of combustion, but when deflagrated with nitre yielded no trace of iron, and were apparently pure carbon. All these forms of carbon are conductors of electricity. (COLQUHOUN, *Ann. of Phil.*, N.S., xii. 50.)

PLUMBAGO. GRAPHITE. BLACK LEAD. This substance must be considered as one of the forms of carbon. It is well known in the manufacture of pencils, for which purpose it is almost exclusively obtained from the mine of Borrowdale, at the west end of Derwent Lake, in Cumberland, where it was first wrought during the reign of Elizabeth*. In a less pure state it is not an uncommon mineral, occurring in detached masses generally in primitive rocks. It is of an iron-gray color, metallic lustre, and soft and greasy to the touch: its specific gravity varies from 1·9 to 2·3; it occasionally occurs crystallized in hexangular plates; it conducts electricity, is infusible; and very difficult of combustion, and is an excel-

* In sawing the Cumberland and other fine varieties of graphite into the small prisms used in pencil-making, a considerable portion is lost in the form of powder: this has usually been sold for the purpose of making anti-attrition applications, and the mixtures used for cleaning or covering cast iron. Mr. Brockedon, however, has ascertained that, under great pressure and exclusion of interstitial air, this powder

may be squeezed into adherent masses as dense and applicable to the same purposes as the original plumbago, and has patented this ingenious invention. Another process of rendering the waste of the pencil-maker available as "artificial black-lead," invented in 1795 by Messrs. Conti and Humboldt, is described at length in Ure's *Dictionary of Arts*, &c. (Art. *Pencil*.)

lent ingredient in crucibles and melting-pots intended to withstand high temperatures, especially when protected by mixture with refractory clay. When it is burned in a stream of oxygen gas, it leaves a small quantity of yellow ash, composed chiefly of oxide of iron, but varying in quantity in different specimens. According to Vanuxen (*SILLIMAN'S Jour.*, x. 105), the following are the components of three varieties of this mineral; the two first are the pure and impure varieties from Borrowdale, and the third a pure specimen from Bustletown, Pennsylvania.

	1.	2.	3.
Carbon	88·37	61·27	95·4
Water	1·23	5·33	0·6
Silica	5·10	10·10	2·6
Alumina	1·00	3·20	0·0
Oxides of iron and manganese....	3·60	20·00	1·4
	<hr/> 99·30	<hr/> 99·90	<hr/> 100·0

Schrader analysed the ashes remaining after the combustion of 200 grains of English and 200 grains of Spanish plumbago, with the following results. (*Ann. of Phil.*, i. 294.)

	Borrowdale.	Spanish.
Protoxide of iron	11·6	14·2
Silica	7·0	3·0
Alumina	4·6	2·4
Oxide of copper	0·0	1·0
Titanic acid	6·3	3·1
	<hr/> 29·5	<hr/> 23·7

It seems probable, therefore, that in plumbago the oxide of iron is in combination with titanic acid and silica, and not with the carbon so as to constitute a *carburet of iron*. Some specimens, indeed, as those from Barreros in Brazil, scarcely contain a trace of iron.

ANTHRACITE. MINERAL CHARCOAL. GLANCE-COAL. The *culm* of Wales, and the *Kilkenny-coal* of Ireland, are species of this mineral. It much resembles common coal in appearance, but is difficult of combustion, and burns without flame, smell, or smoke, and leaves very little ash. Its specific gravity is about 1·4.

Coke is the carbonaceous residue of the distillation of pit-coal; it has a porous texture, and more or less lustre, frequently appearing metallic; in small fragments it is very difficult of combustion in the flame of a candle, but when employed in large masses as fuel, it produces an intense and steady heat. It varies extremely in purity, but when carefully prepared from the purest varieties of coal, it leaves little residue after combustion.

Such are the principal varieties of carbon: the diamond appears to be this element in its purest form, for it mostly burns away without residue, and affords scarcely any appreciable traces of foreign matter: the other forms of carbon, on the contrary, yield indications of extraneous substances, such as oxygen, nitrogen, hydrogen, or metals, or their oxides. They are all infusible, and the porous varieties are very bad conductors of heat; with the exception of the diamond, they conduct electricity, but some of them more perfectly than others, and plumbago and very dense

and well-burned wood-charcoal almost rival some of the metals in this respect; this circumstance, and the strong lustre of some of the species of charcoal, seem almost to justify Döbereiner in placing it among the metals under the name of *Carbonium*. Berzelius describes diamond, graphite, and charcoal, as three allotropic modifications of carbon, distinguishing them by the symbols Ca , $C\beta$, and $C\gamma$.

The accurate determination of the atomic weight of carbon is a matter of much importance, and is now, consistently with Dr. Prout's original views, almost universally admitted to be $\equiv 6$ on the hydrogen scale. The elaborate experiments of Dumas and Stas have further sanctioned the entire accuracy of this equivalent, so that the fractional numbers 6.13 (or 76.4 upon the oxygen scale), and 6.05 adopted by Berzelius and others, will probably fall into disuse.

CARBON AND OXYGEN. Though these substances possess for each other a very powerful affinity, they do not combine at common temperatures: to this remark, however, there are, perhaps, some exceptions, and it appears that certain forms of carbon may exist, which produce carbonic acid whenever they come into contact with oxygen; these are, probably, peculiar to organic combinations.

The only binary compounds of carbon and oxygen which can be isolated, are carbonic oxide $= CO$, and carbonic acid $= CO_2$; there are many other hydrated or hydracids which may be hypothetically derived from these, and especially the oxalic acid $= C_2O_3, HO$, or CO, CO_2, HO or $C_2O_4 + H$, but these are reserved for further consideration, more especially amongst organic compounds.

CARBONIC OXIDE. GASEOUS OXIDE OF CARBON. CO . This gas, which was discovered by Priestley (*Obs. on Air*, i. 298), may be obtained by subjecting *carbonic acid* to the action of substances which abstract a portion of its oxygen. Upon this principle it is produced by heating, in an iron retort, an intimate mixture of carbonate of lime (chalk) and charcoal: $CaO, CO_2 + C = CaO + 2CO$: or of equal weights of chalk and iron or zinc filings, $CaO, CO_2 + Zn = CaO + ZnO + CO$. It is also obtained by heating a mixture of equal parts of oxide of zinc and charcoal; but the mixture which in this way is said to afford it most pure is equal parts of carbonate of baryta and clean iron filings; these should be introduced into a small earthen retort, so as nearly to fill it, and exposed to a red heat: the first portion of gas being rejected as mixed with the air of the retort, it may afterwards be collected nearly pure: it should be washed with lime-water, and may afterwards be preserved over water. Carbonic oxide may also be obtained by gently heating oxalic acid with five or six times its weight of sulphuric acid; the mixture effervesces in consequence of the evolution of equal volumes of carbonic oxide and carbonic acid gas; the latter may be abstracted by a caustic alkaline solution, and pure carbonic oxide gas remains. (DUMAS, *Edinburgh Journal of Science*, vi. 350.) In this case the evolution of carbonic oxide and acid is caused by the abstraction of water from oxalic acid which contains in its anhydrous state the elements of 1 atom of carbonic oxide and 1 atom of carbonic acid; but these can only exist as oxalic acid when in union with water, or with a base, anhydrous oxalic acid not having been isolated. Crystallised oxalic acid is

$= \text{C}_2\text{O}_3, 3\text{HO}$, which acted upon by 3 atoms of oil of vitriol $= 3 [\text{SO}_3, \text{HO}]$ becomes $3 [\text{SO}_3, 2\text{HO}] + \text{CO}_2 + \text{CO}$; the hydrated sulphuric acid remains in the retort, the carbonic acid is abstracted by passing the gases through a solution of caustic potassa, and the carbonic oxide passes off. Another source of carbonic oxide, suggested by Fownes (*Mem. Chem. Soc.*, i. 251), is the action of 10 parts of concentrated sulphuric acid on 1 part of pulverised crystals of ferrocyanide of potassium; the gas thus obtained is pure and evolved in the proportion of 300 cubic inches from half an ounce of the salt. Ferrocyanide of potassium contains cyanide of potassium $= \text{K}, \text{C}_2\text{N}$, and cyanide of iron $= \text{Fe}, \text{C}_2\text{N}$: they are converted by the oil of vitriol into sulphates of potassa and of iron, sulphate of ammonia, and carbonic oxide: thus, in regard to the cyanide of potassium, $\text{K}, \text{C}_2\text{N} + 2 [\text{SO}_3, \text{HO}] + 2\text{HO} = \text{KO}, \text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 2\text{CO}$. It not unfrequently happens that carbonic oxide is formed by the combustion of carbon when the supply of oxygen is inadequate to the production of carbonic acid: hence the lambent blue flame which sometimes plays upon a coke or charcoal fire, or is seen to issue from certain furnaces: this is in fact passing carbonic acid over red-hot charcoal; so that $\text{CO}_2 + \text{C}$ becomes 2CO .

The nature of carbonic oxide was first made known by Cruickshank, in 1802 (*NICHOLSON'S 4to Journal*, v.); and about the same time it was examined by Clement and Desormes. (*Ann. de Chim.*, xxxix. 26.)

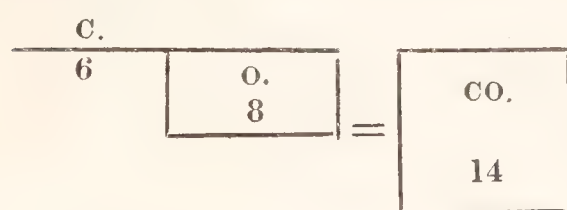
The specific gravity of this gas compared to hydrogen is as 14 to 1; and to atmospheric air as 0.9706 to 1.0000; 100 cubical inches weighing 29.0979 grains. (At the temperature of 32° 100 cubic inches weigh 31.8790 grains. THOMSON.) It is very fatal to animals, and produces giddiness and fainting when respired mixed with atmospheric air. (*Phil. Mag.*, xliii. 367.) When breathed pure, it almost immediately produces profound coma. It extinguishes flame, and burns with a peculiar blue light, when mixed with, or exposed to, atmospheric air. Sir H. Davy found that the temperature of an iron wire heated to dull redness was sufficient to inflame it. It has no taste and little odor, it does not affect vegetable colors, occasions no precipitate in lime water, and is very sparingly absorbed by water which has been deprived of air. When burned under a dry bell-glass of air or oxygen, no moisture whatever is deposited, showing that it contains no hydrogen. Carbonic acid is the only result of this combustion.

Carbonic oxide suffers no change by being passed and repassed through a red-hot porcelain tube; nor is it decomposed at high temperatures by phosphorus, sulphur, nor even, according to the experiments of Saussure, by hydrogen (*Journal de Physique*, lv.), though it is stated, upon other authorities, that at high temperatures hydrogen does decompose it. When 1 volume of carbonic oxide is detonated with 1 of nitrous oxide, there result 1 volume of carbonic acid and 1 of nitrogen. (HENRY, *Ann. of Phil.*, N. S., viii. 299.) On this principle is founded a method of ascertaining the purity of nitrous oxide, it being implied, that that gas is free from nitric oxide. Let a given volume, say 100 measures, be exploded with slight excess of carbonic oxide,—if the nitrous oxide be pure, 100 measures of carbonic acid should be produced, and whatever is short of that proportion may be ascribed to impurity. None of the metals exert any action upon this gas, except potassium and sodium, which, at a red-heat, burn in it by abstracting its oxygen, and carbon is deposited.

Dr. Henry found, that when a mixture of carbonic oxide with more than half its volume of oxygen is exposed over mercury in contact with spongy platinum, to a temperature between 300° and 310° , it begins to be converted into carbonic acid, and, at a heat a few degrees higher, is quickly acidified. At common temperatures these mixtures are very slowly acted on. When carbonic oxide is added in an equal volume to a mixture of hydrogen and oxygen gases in explosive proportions, it prevents spongy platinum from causing detonation; but the gases slowly act on each other, and form water and carbonic acid. The platinum occasions mixtures containing less carbonic oxide to explode. (*Phil. Trans.*, 1824, p. 271.)

The composition of carbonic oxide is determined by the result of its combustion with oxygen, with which it forms carbonic acid. When *two* volumes of carbonic oxide and *one* of oxygen are acted on by the electric spark*, detonation ensues, and *two* volumes of carbonic acid are produced: hence it follows, that carbonic oxide contains half as much oxygen, and *the same* quantity of carbon, as carbonic acid, and assuming carbonic oxide to be a *protoxide of carbon*, it will consist of

Gay Lussac.						Volumes.	Sp. Gr.
Carbon	1	6	42.86	43.	Carbon vapor	1.0	0.4160
Oxygen.....	1	8	57.14	57.	Oxygen gas	0.5	0.5546
<hr/>						<hr/>	<hr/>
Carbonic oxide	1	14	100.00	100.		1	0.9706



As carbon cannot be converted into vapor, its density in that state cannot of course be experimentally determined, and therefore any assumption as to its combining *volume* must be purely hypothetical. But, since car-

bonic oxide consists of 6 parts of carbon and 8 of oxygen by weight, (1 atom and 1) and carbonic acid, of 6 of carbon and 16 of oxygen (1 atom and 2); and assuming the combining volume of carbon vapor to be the same as that of hydrogen gas; then, in carbonic oxide there would be 2, and in carbonic acid 1 volume of carbon vapor united with 1 of oxygen, and the sp. gr. of oxygen to that of carbon vapor would be as 16 to 6, or 1.1092 to 0.416, as represented in the above table. If, on the other hand, as Mitscherlich suspects, the combining volume of carbon vapor be the same as that of oxygen gas (namely, half that of hydrogen) then carbonic oxide gas would contain equal volumes of oxygen and carbon vapor, and carbonic acid, 2 and 1, in which case the sp. gr. of oxygen to carbon vapor would be as 8 to 6, or 1.1092 to 0.832. It is, however, possible that the combining volume of carbon vapor may be less or more than that thus assumed.

Carbonic oxide is sometimes represented as performing the part of an elementary base; uniting, for instance, with oxygen to form carbonic, and oxalic acids; with chlorine to form chlorocarbonic acid; and with amide to form oxamide; hence, in regard to *oxalic acid*, the term *oxalyle* proposed for it by Berzelius.

* The combustion may be effected in the common detonating tube, (fig. 265,) or in Ure's Eudiometer, (fig. 281,) or in the detonator, (fig. 266.) In the latter case the light evolved is extremely brilliant.

CARBONIC OXIDE AND CHLORINE. OXYCHLORIDE OF CARBON. CHLOROCARBONIC OR CHLOROXICARBONIC ACID. PHOSGENE GAS. CO_2Cl_2 . This gas was obtained by Dr. J. Davy (*Phil. Trans.*, 1812, p. 144), by exposure to solar light of a mixture of equal volumes of chlorine and carbonic oxide: hence its name, from $\phi\omega\varsigma$, *light*, and $\gamma\epsilon\nu\nu\alpha\omega$, to *produce*. It is also formed by exposing the mixed gases to ordinary daylight, but several hours are required for the purpose. When perfectly excluded from light these gases exert no mutual affinity. In the sunshine the mixture diminishes in bulk to half its original volume, and forms a compound of a very peculiar and pungent odor, but not disagreeable when considerably diluted. It reddens litmus; is soluble in water, and resolved by it into *carbonic and hydrochloric acid gases*. Alcohol and pyroxylic spirit absorb it, and form peculiar ethereal compounds. The specific gravity of chlorocarbonic acid to hydrogen is as 50 to 1, and to common air as 3.425 to 1. 100 cubical inches weigh about 106 grains: at 32° , 100 cubical inches weigh 113.85 grains. (THOMSON.)

When tin or zinc are heated in one volume of this gas, they abstract and combine with the chlorine, and evolve one volume of carbonic oxide. When potassium is heated in it, potassa and chloride of potassium are formed, and carbon evolved. It does not detonate by the electric spark either with oxygen or hydrogen singly, but if mixed with 1 volume of hydrogen and 0.5 volume of oxygen, it explodes, yielding carbonic and hydrochloric acids. Phosphorus and sulphur may be sublimed in it without change. It consists of

Carbon.....	1	6	12	} = {	Carbonic oxide	1...14...28...	1...0.9706		
Oxygen	1	8	16		Chlorine	1...36...72...	1...2.4543		
Chlorine	1	36	72						
<hr/>						<hr/>	<hr/>	<hr/>	<hr/>
Chlorocarbonic acid	1	50	100			1 50 100	1 3.4249		

Chlorocarbonic acid, in reference to the theory of substitutions, has been regarded as carbonic acid in which 1 equivalent of oxygen is replaced by 1 of chlorine. H. Rose represents it as a carbonate of bichloride of carbon $= \text{CO}_2\text{CCl}_2$. (*Poggend.*, Lii. 77.)

CHLOROCARBONATE OF AMMONIA. $2\text{NH}_3\text{CO}_2\text{Cl}$. Chlorocarbonic acid condenses 4 volumes or 2 atoms of ammonia, producing a peculiar deliquescent compound of a white color, which is resolved by the action of water into hydrochlorate and carbonate of ammonia. This salt is also decomposed by sulphuric, nitric, and hydrochloric acid, which evolve from it 2 volumes of hydrochloric and 1 volume of carbonic acid; it dissolves without effervescence in acetic acid, and sublimes unaltered, when heated in carbonic or sulphurous acid gas. (J. DAVY.) It dissolves in alcohol, but not in ether. (REGNAULT.) Its components are

Carbon	1	6	7.2	}	Chlorocarbonic acid	1	50	59.5
Oxygen	1	8	9.5					
Chlorine	1	36	42.8					
Hydrogen	6	6	7.2	}	Ammonia.....	2	34	40.5
Nitrogen	2	28	33.3					
	<hr/>	<hr/>	<hr/>				<hr/>	<hr/>
	1	84	100.0			1	84	100.0

According to Regnault (*Ann. Ch. et Ph.*, Lxix. 180), this compound contains sal-ammoniac and a compound of carbonic oxide and amidogen,

or *carbamide*, which, however, has not been isolated; for 1 atom of chlorocarbonic acid and 2 atoms of ammonia contain the elements of carbamide and hydrochlorate of ammonia (or chloride of ammonium), $\text{CO}, \text{Cl} + 2 \text{NH}_3 = \text{CO}, \text{NH}_2 + \text{NH}_4\text{Cl}$.

CARBAMIDE, therefore, is a compound of

Carbon.....	1	6	20.0	} = 1 Carbonic oxide	14	46.8
Oxygen	1	8	26.8			
Nitrogen	1	14	46.6			
Hydrogen	2	2	6.6	} = 1 Amidogen	16	53.2
<hr/>						
Carbamide	1	39	100.0		30	100.0

CARBONIC ACID. FIXED AIR. AERIAL ACID. CO_2 . This important compound was first described by Dr. Black, in 1757, under the name of *fixed air*, in his inaugural dissertation on magnesia. It is produced by burning carbon, either pure charcoal, or graphite, or the diamond, in oxygen gas; the oxygen is thus becoming converted into carbonic acid gas, suffers no change of bulk, so that the quantity of carbon in carbonic acid may be learned by comparing its weight with that of an equal volume of pure oxygen.

Combustion of the Diamond. The combustibility of the diamond seems first to have occurred to Newton. In the year 1694 the Florentine Academicians verified his anticipations, and proved its destructibility by heat by means of a burning lens. The *products* of its combustion were first examined by Lavoisier, in 1772, and subsequently with more precision by Guyton Morveau, in 1785. (*Ann. de Chim.*, xxxi.) In 1797, (*Phil. Trans.*,) Tennant demonstrated the important fact, that when equal weights of diamond and pure charcoal were submitted to the action of red-hot nitre, the results were in both cases the same: and, in 1807, (*Phil. Trans.*,) the combustion of the diamond in pure oxygen was found by Allen and Pepys to be attended with precisely the same results as the combustion of pure charcoal.

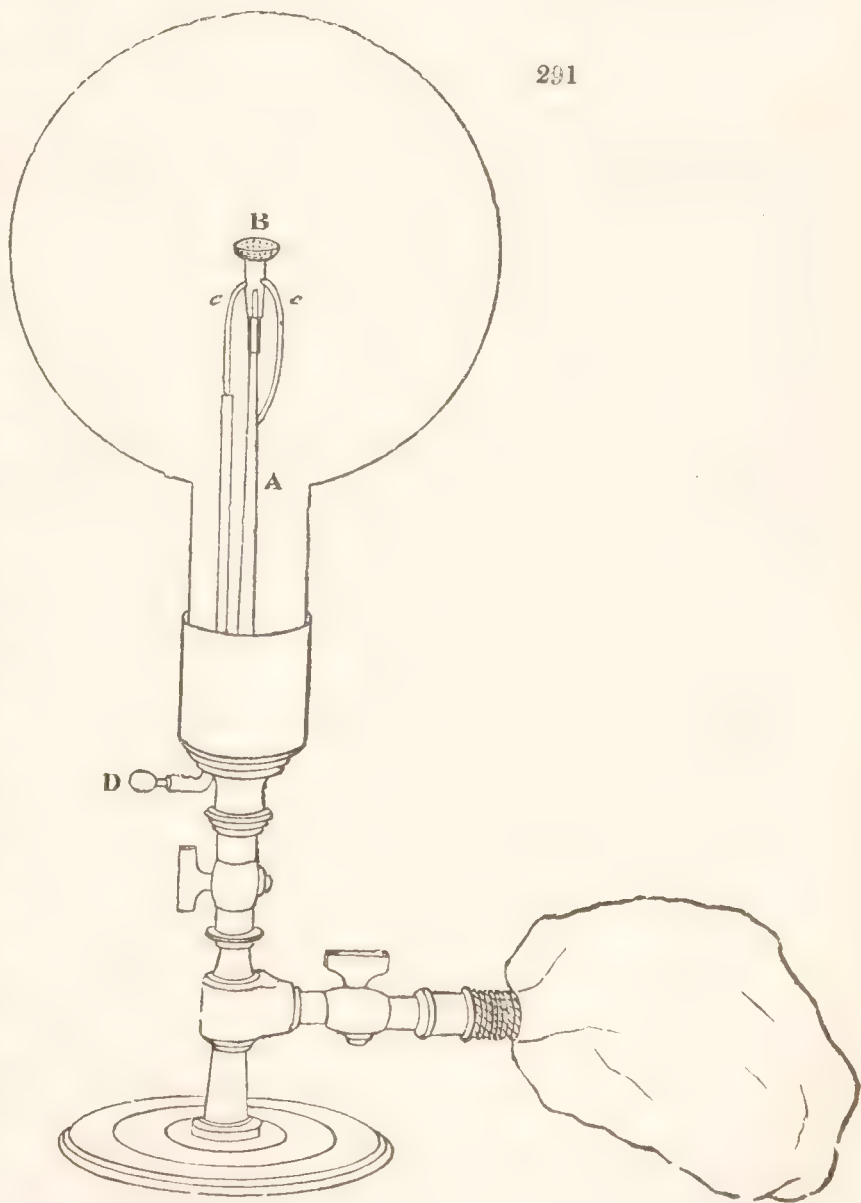
When the diamond is heated in the flame of the blow-pipe it soon begins to burn, and the combustion continues as long as the temperature is sufficiently high, but it does not produce heat enough, during its combination with the oxygen of the atmosphere, to maintain its combustion. If, whilst thus burning, it be introduced into a jar of pure oxygen, the combustion continues longer, and sometimes till the whole is consumed: the best support for it, in this experiment, is a small loop of platinum wire, or a very small and thin platinum spoon, perforated with many holes; in this it may first be intensely heated by the oxygen blow-pipe, and whilst burning, carefully immersed into a bottle of pure oxygen gas containing a little lime-water: a good cork, through which the wire of the spoon passes, should secure the mouth of the bottle: it will thus go on burning brilliantly for some time, and the formation of carbonic acid be shown by the milkiness of the lime-water. In securing the fragment of diamond for this experiment in the loop of platinum wire, care must be taken to select the latter of proper diameter: if too thin, the intense heat produced during the combustion is apt to fuse it; and if too thick, it extinguishes the diamond by its cooling or heat-conducting power. A small prismatic piece of pure graphite, such as is used for pencils, or of

pure and hard charcoal may be similarly burned with the same results. As regards the graphite, it will be found that it is nearly as difficult of combustion as the diamond: it should be carefully annealed previous to ignition, by cautiously heating it in the flame of a spirit-lamp, when it will generally endure a white-heat without splintering into fragments.

The combustion of the diamond may also be effected by placing it upon a proper platinum capsule in a jar of pure oxygen inverted over mercury, and throwing upon it the focus of a burning lens. Sir H. Davy, when at Florence, in 1814 (*Phil. Trans.*, 1814, p. 558), used for this purpose the lens employed in the first trials on the action of solar heat on the diamond, instituted by Cosmo III., Grand Duke of Tuscany: he found that the diamond continued to burn in the oxygen, after being withdrawn from the focus, with so brilliant a light as to be visible in the brightest sunshine, and with very intense heat.

The following is another form of apparatus which may be employed for exhibiting the results of the combustion of the diamond. It consists

of a glass globe, of the capacity of about 140 cubical inches, furnished with a cap, having a large aperture; the stop-cock, which screws into this cap, has a jet A, rising from it, nearly into the centre of the globe; this is destined to convey a small stream of hydrogen. Two wires, *c c*, terminate at a very little distance from each other, just above this jet, and are intended to inflame the stream of hydrogen by electrical sparks; one of them commences from the side of the jet, the other is enclosed and insulated nearly in its whole length in a glass tube: the tube and wire pass through the upper part of the stop-cock, and the wire terminates on the out-

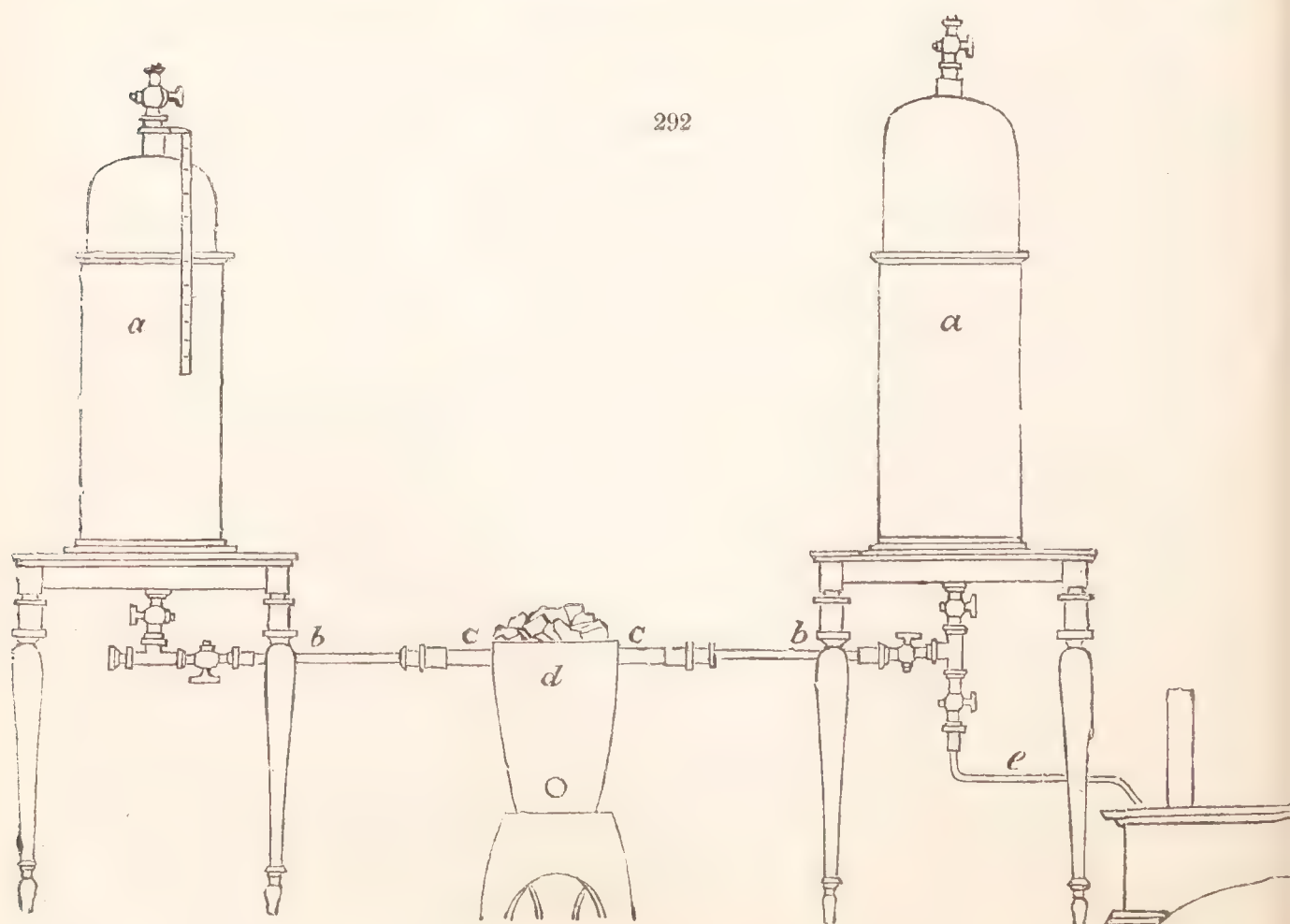


side in a ball or ring *D*, at which sparks are to be taken from the machine, either directly or by a chain. On the end of the jet is fixed, by a little socket, a small capsule *B*, made of platinum-foil. This capsule is pierced full of small holes, and serves as a grate to hold the diamonds. Its distance is about three-quarters of an inch from the end of the jet; and the arm by which it is supported is bent round, so that the stream of hydrogen shall not play against it. The stop-cock screws by its lower

termination on to a small pillar, fixed on a stand, and at the side of this pillar is an aperture, by which a bladder filled with hydrogen gas may be connected with the apparatus.

On using the apparatus, the diamond is to be placed in the capsule; and then the globe being screwed on to the stop-cock, the latter is to be removed from the pillar and placed on the air-pump; the globe is then to be exhausted, and afterwards filled with pure oxygen; or, lest the stream of oxygen in entering should blow away the diamond, the globe may be filled with the gas first, and then, dexterously taking out the stop-cock for a short time, the diamond may be introduced, and the stop-cock replaced. The apparatus is then to be fixed on the pillar, and a bladder of hydrogen gas attached to the aperture. Now, passing a current of sparks between the wires, a small stream of hydrogen is to be thrown in, which inflaming, immediately heats the diamond and capsule white-hot; the diamond will then enter into combustion, and the hydrogen may be immediately turned off and the bladder detached. The diamond will continue to burn, producing a strong white heat, until so far reduced in size as to be cooled too low by the platinum with which it lies in contact. When the flame of hydrogen is used to heat the diamond, it is evident a little water will be formed in the globe, but this is of no consequence except in attempts to detect hydrogen in the diamond; the inconvenience may in that case be obviated by using the flame of carbonic oxide. As, however, no hydrogen has at any time been detected in the diamond, it is better to use that gas as the heating agent: for then the carbonic acid, produced by the combustion, is unmixed with that from any other source.

The following method of illustrating the products of the combustion of the diamond was employed by Allen and Pepys (*Phil. Trans.*, 1807): *a a* are mercurial gasometers, one of which is filled with pure oxygen gas.

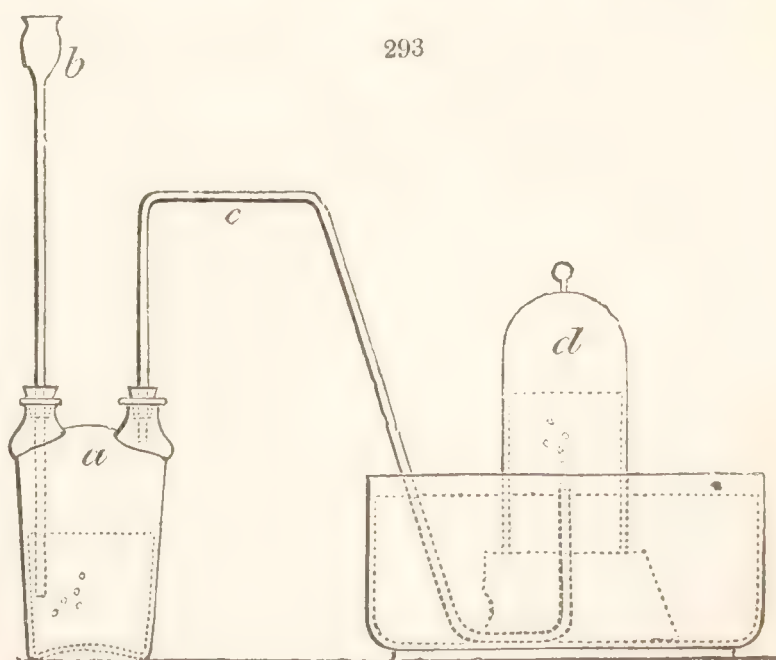


The brass tubes *b b*, properly supplied with stop-cocks, issue from the gasometers, and are connected with the platinum tube *c c*, which passes through the small furnace *d*. *e* is a glass tube passing into the mercurio-pneumatic apparatus, by which the gas may be drawn out of the gasometers into convenient receivers. A given weight of diamond is introduced into the centre of the platinum tube, which is then heated to bright redness, and the gas passed over it, backwards and forwards, by alternately compressing the gasometers. Carbonic acid is soon formed, and it is found that the increase of weight sustained by the oxygen is equivalent to that lost by the diamond; that the oxygen undergoes no change of bulk; and that the results are, in other respects, similar to those obtained by the combustion of perfectly pure charcoal, or of graphite, similarly burned.

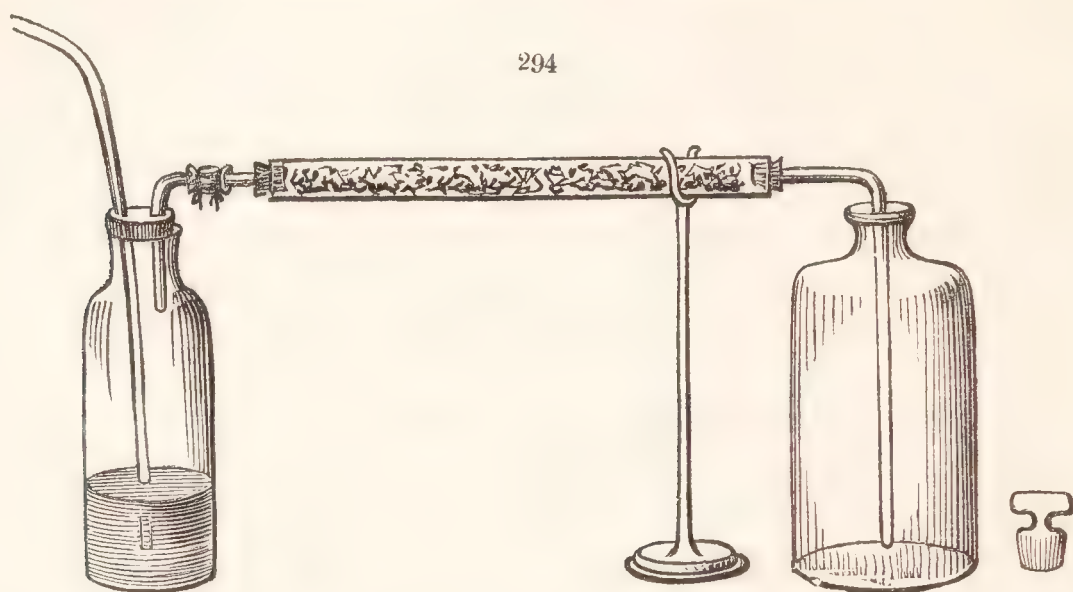
When *charcoal* is burned in a jar of oxygen gas, the phenomena of the combustion very much depend upon the nature of the charcoal, which, if well made, and of a dense wood, glows with intense heat and gradually disappears, but if of a lighter wood, and especially if covered with portions of the bark, throws off jets of brilliant sparks, and furnishes one of the most striking experiments. These scintillations are especially brilliant and beautiful when a small piece of the charred bark of oak or elm is used; it should be attached to a copper wire and introduced into a sufficiently capacious air-jar filled with pure oxygen; the combustion may thus be made to last for some minutes, and is often attended by slight explosions which sometimes so suddenly expand the gas as to elevate the jar and risk its fracture if not attended to. If the quiet combustion of the charcoal is only required for the purpose of showing the conversion of the oxygen into carbonic acid, the best kind of carbon which can be used is that obtained from box, *lignum vitæ*, or other hard and dense wood.

Preparation, Liquifaction, and Solidification of Carbonic Acid Gas.—

For all the common purposes of experiment, carbonic acid is best procured by the action of dilute hydrochloric acid upon white marble, which, in small fragments, is introduced into the two-necked bottle *a*, and covered with water; hydrochloric acid is then slowly poured down the funnel *b*, which causes an immediate effervescence, and the gas passes through the bent tube *c*, into the inverted jar *d*. When the action ceases, it may be renewed by the addition of fresh acid, until the whole of the marble is dissolved. When large quantities of carbonic acid are required, chalk and dilute sulphuric acid are generally resorted to, and for some particular purposes bicarbonate of soda and dilute sulphuric acid are used. When required pure and dry, the tube *c* must pass into a



washing-bottle, and the gas, as it issues thence, be conveyed through a long chloride of calcium tube to deprive it of moisture; it may then be conducted to the bottom of a dry stopper-bottle to be filled by displacement, as in the arrangement shown in figure 294.



Liquid Carbonic Acid. At all common temperatures and pressures carbonic acid retains the gaseous state, but when duly subjected to great pressure, it becomes liquid. To effect its liquifaction, Faraday proceeded as follows: A strong tube, (see fig. 95,) of about one-fourth of an inch diameter and eight inches long, being bent, at about two inches from its end, to an obtuse angle, and sealed at the shorter end, sulphuric acid was poured in through a small funnel, so as not to soil the larger leg, which was then loosely filled with fragments of carbonate of ammonia, and also hermetically sealed; the acid was then made to run upon the salt, and the evolved carbonic acid gradually appeared, coerced into the liquid form. The utmost precautions are here necessary to guard against explosion: such as goggles and a glass mask to preserve the face and eyes, and thick gloves for the hands: the tubes should also never be touched without great care; for sometimes, after having held the fluid safely for weeks together, they have exploded from some very slight increase of temperature. (*Phil. Trans.*, 1823.)

The liquifaction of carbonic acid is now conducted upon a large scale, especially by Mr. Addams of Kensington, who sometimes has treasured up, in suitable reservoirs, as much as nine gallons at one time, and has even made it an article of commerce, supplying it for the use of the experimentalist at a moderate charge, and in any required quantity, together with the necessary apparatus for collecting it in the solid form.

The apparatus he employs is of two kinds: the first, or simple mode, is dependent upon the chemical forces disengaging the carbonic acid from the materials used, under confinement, as originally suggested by Faraday; and in this, the general construction of the instruments employed is similar to those of M. Thilorier (*Ann. Ch. et Ph.*, LX. 427), although in respect to form, material, and structure of the valves, there is considerable difference, being more simple in arrangement, and lighter in proportion to strength.

The second, or improved method, is partly dependent upon the chemical forces, and partly effected by mechanical compression with powerful pumps.

For either process two strong *wrought iron* vessels are required, one is named the *generator*, A (fig. 295), the other the *receiver*, B; each of these vessels is a cylinder two feet long and four inches internal diameter, having hemispherical ends, and of such strength as to bear proving to more than 4000 lbs. upon a square inch.

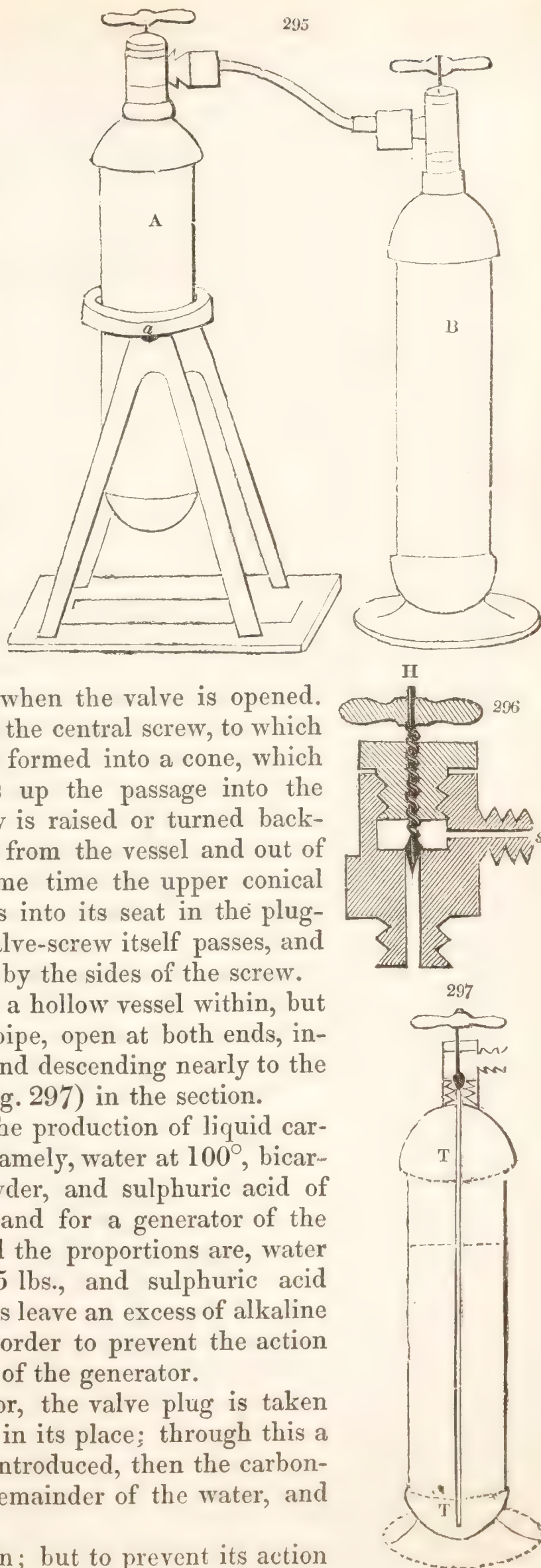
The generator is furnished with an axis *a*, and mounted upon a cast iron frame so as to revolve in a vertical plane *aa* (fig. 299). At one end of each vessel is screwed on a peculiar valve (fig. 296), so constructed as to prevent leakage in the screw part, when the valve is opened. The lower, or valve part, of the central screw, to which the handle *H* is applied, is formed into a cone, which when screwed down shuts up the passage into the vessel; but when the screw is raised or turned backwards, there is a passage from the vessel and out of the side vent *s*; at the same time the upper conical shoulder of the valve comes into its seat in the plug-piece through which the valve-screw itself passes, and thus prevents escape of gas by the sides of the screw.

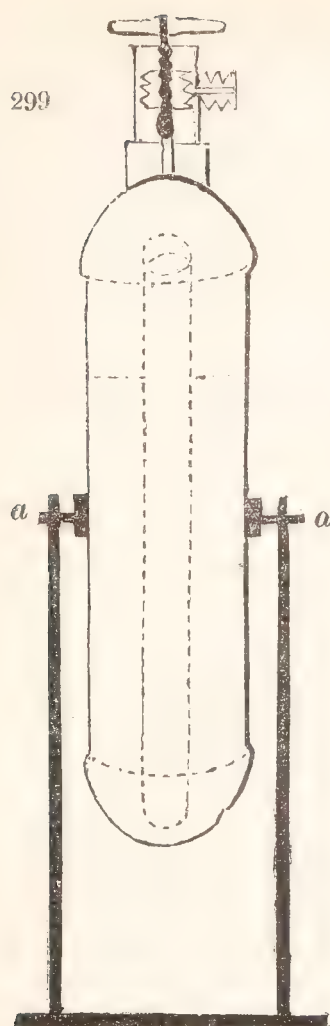
The *generator* is simply a hollow vessel within, but the *receiver* has a slender pipe, open at both ends, inserted into the valve-plug, and descending nearly to the bottom, as shown by *TT* (fig. 297) in the section.

The materials used in the production of liquid carbonic acid are as follows: namely, water at 100° , bicarbonate of soda in fine powder, and sulphuric acid of full commercial strength; and for a generator of the dimensions before described the proportions are, water 6.25 lbs., bicarbonate 2.75 lbs., and sulphuric acid 1.47 lbs. These proportions leave an excess of alkaline salt, which is desirable in order to prevent the action of the acid upon the metal of the generator.

To charge the generator, the valve plug is taken out, and a funnel inserted in its place; through this a part of the tepid water is introduced, then the carbonate, and afterwards the remainder of the water, and then stirred with a rod.

The acid is next put in; but to prevent its action





before the valve plug is replaced, it is contained in a brass tube (fig. 298), of such diameter and length as to hold the measure of acid and also pass through the orifice in the neck of the generator, and to stand erect with its open end above the saline mixture within, as shown in fig. 299. The valve-plug is now firmly screwed to the generator, and the whole inverted and turned over and over, by which the acid comes into contact with the carbonate of soda, and the mixture is completely effected. Then by allowing the generator to stand a few minutes erect, with the valve end upwards, the liquified carbonic acid, being lighter than the resulting sulphate of soda, rises, and floats as a distinct stratum. A connection is then made between the generator and *receiver* by an union pipe, as shewn in figure 295, and then the valves of both vessels being opened, the carbonic acid passes, by a process of rapid distillation, from the former into the latter. This transfer is accelerated in proportion as the temperature of the two vessels differs; hence warm water is employed

in charging; an increase of heat also ensues by the acid mixing with the water; the receiver also should be put into cold or iced water.

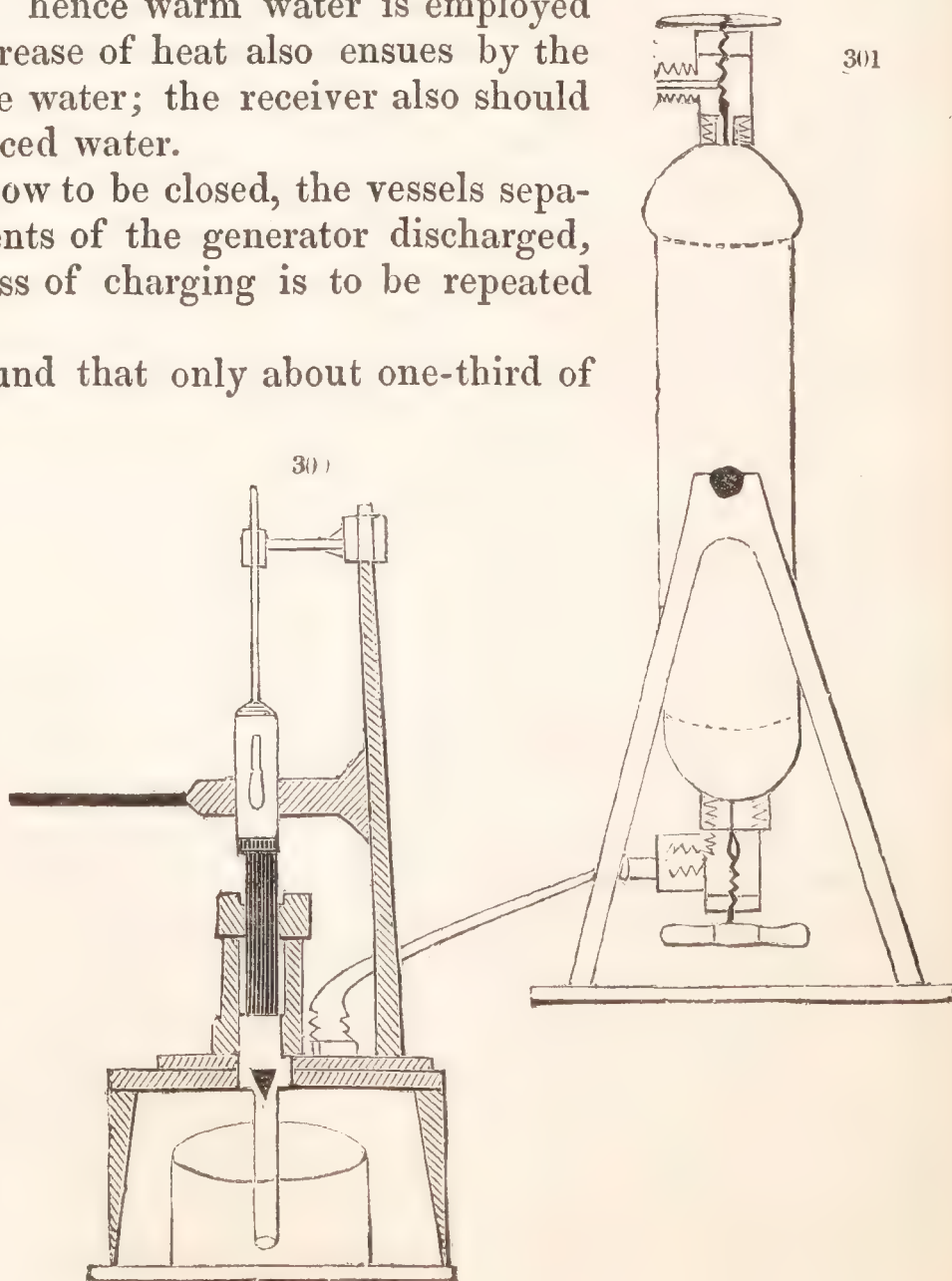
The valves are now to be closed, the vessels separated, and the contents of the generator discharged, and the same process of charging is to be repeated many times.

Mr. Addams found that only about one-third of the carbonic acid of the generator passed into the receiver in the ordinary management of this process; he was, therefore, led to construct a pump (fig. 300), to force water into the lower end of a generator, equipped with two valves (fig. 301), and thus by filling the generator, the whole of the liquid carbonic acid is transferred into the receiver,

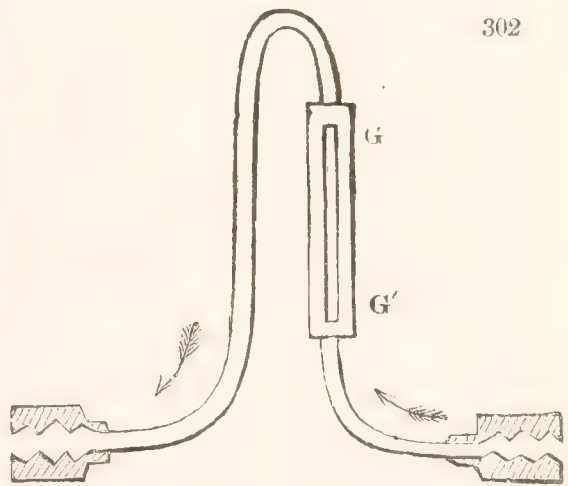
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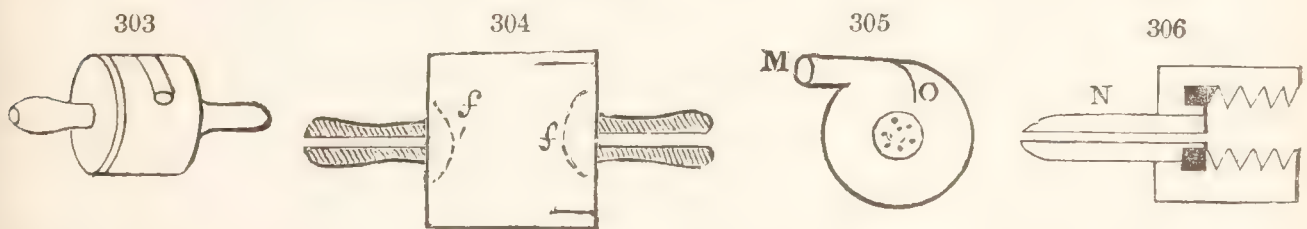


and that too without the cooling of the receiver with ice; and by this plan an economy equal to two-thirds in material and time is effected. But in order to use a pump it was necessary to contrive a gauge to observe when the generator was filled and all the carbonic acid displaced. The gauge for this purpose is shown (inserted in the union-pipe) at G G', fig. 302. It consists, essentially, of a strong glass tube, secured within a metal cylinder formed by boring out the centre of the solid: this last has slits cut parallel to its length on opposite sides; then as the passage into the receiver is through this glass gauge, it is easy to observe the instant when the saline fluid of the generator rises into it, and then to stop the action of the pump; and, consequently, no liquid but the carbonic acid enters the receiver.



Mr. Addams has also attached a gauge of similar construction to a double-valved *receiver*, and with it is enabled to see the carbonic acid at any time, to measure the quantity transferred from this vessel into others, and to obtain certain useful information respecting the quantity produced by different modes of management.

Within the receiver, when charged, there is liquid carbonic acid below, and highly condensed gas above it: upon opening the valve the expansion of the gas forces the liquid up the central tube T T (fig. 297), and then a part of it instantly passes into the state of gas at the orifice of the outlet s (fig. 296), and another portion is frozen into a white snow-like solid, affording a beautiful instance of the sudden transference of heat when a liquid expands into a gas. This white matter, or *solid carbonic acid*, is blown out in finely-divided particles, and to collect it, an ingeniously constructed recipient or *draw-out box* is used, being the contrivance of M. Thilorier. It consists of a brass cylindrical case (fig. 303), having tubular handles affixed to its ends. Plates of pierced brass are fixed before the outlet of each handle, as shown by ff (fig. 304); these act as sieves to keep back the solid acid and allow the gas to pass out.



The box has a short tube joined to the side, as in section fig. 305, M, so as to form a tangent to the inner circle of the case, and opposite to this tube is placed a bent plate of brass, o, in order to prevent the violence of the intruding gas from blowing the solid matter into such fine powder as would enable it to pass through the perforated discs. For the purpose of taking out the solid, the box is made separable by one end sliding a little within the other, and retainable together by two obliquely grooved holders placed on opposite sides of the joint. This draw-out box is united to the receiver by the union-piece (fig. 306), the nozzle N,

having a small hole through it, and upon this the tangent-tube of the box fits.

From 2·75 lbs. of bicarbonate of soda of average quality, Mr. Addams obtains about 19000 cubic inches of carbonic acid of ordinary pressure and temperature: by the first method, without the pump, 13000 of these are left in the generator, and, of course, escape on opening, unless the receiver be kept colder and a longer time allowed for the transfer than is convenient in a general way of management. He finds that about 12·5 cubic inches of liquid carbonic acid are conveyed into the receiver from each charge of the generator, provided the temperature of the receiver be at 54°. But when the pump is employed the only loss of acid is that which is entangled with the sulphate of soda, and which generally measures 1100 cubic inches, under atmospheric pressure; and in this way about 37 cubic inches of liquid carbonic acid are sent into the receiver, at each charging, instead of 12·5.

The tension of carbonic acid gas as it exists above the liquid depends upon the temperature, and Mr. Addams has given the pressures through a considerable range of the thermometer, namely, from zero to 150°, at intervals of each 5°. The following table includes the force for each successive 10th degree; by which it will be seen, that, similar to vapors of all kinds resting upon their respective liquids, the tension increases in a higher ratio than the temperatures. He employed a pressure gauge of 43 inches in length, in the experiments which afforded data for this table; and many of the results were confirmed by a kind of loaded safety valve. In this table the atmospheric pressure is assumed to be = 15 lbs.

Tempera- ture.	Pressure in lbs. per sq. inch.	Pressure in Atmospheres per sq. inch.	Tempera- ture.	Pressure in lbs. per sq. inch.	Pressure in Atmospheres per sq. inch.
Zero	270·9	18·06	80°	741·3	49·42
10°	300·	20·	90	837·6	55·84
20	346·65	23·11	100	934·8	62·32
30	398·1	26·54	110	1040·25	69·35
40	457·35	30·49	120	1151·7	76·78
50	520·05	34·67	130	1264·65	84·31
60	586·35	39·09	140	1379·55	91·97
70	658·05	43·87	150	1495·65	99·71

Faraday observes, “that the estimates of the pressure of carbonic acid vapor are sadly at variance; thus, Thilorier says, it has a pressure of 26 atmospheres at 4°, whilst Addams says, that for that pressure it requires a temperature of nearly 30°. At 50° Brunel estimates the pressure as 60 atmospheres, whilst Addams makes it only 34·67. The following are the pressures which I have recently obtained.” (*Phil. Trans.*, 1845, 166.) The marked numbers are from *experiments*.

Fahrenheit.	Atmospheres.	Fahrenheit.	Atmospheres.	Fahrenheit.	Atmospheres.
* — 111°	1·14	— 60°	6·97	* — 4°	21·48
— 110	1·17	* — 56	7·70	0	22·84
* — 107	1·36	— 50	8·88	* 5	24·75
— 100	1·85	— 40	11·07	* 10	26·82
* — 95	2·28	* — 34	12·50	* 15	29·09
— 90	2·77	— 30	13·54	20	30·65
* — 83	3·60	* — 23	15·45	* 23	33·15
— 80	3·93	— 20	16·30	30	37·19
* — 75	4·60	* — 15	17·80	* 32	38·50
— 70	5·33	— 10	19·38		

Liquid Carbonic Acid is limpid, colorless, and extremely fluid. Its specific gravity at 32° is 0.83: it distils readily and rapidly at the difference of temperature between 32° and 0° . Its refractive power is much less than that of water. Mr. Brunel endeavoured to apply this liquid as a mechanical agent for the production of motive power: of this attempt a short account will be found in the *Quarterly Journal* (Old Series, xxi. 131). It exhibits a remarkable property in respect to its expansibility by heat, in which it appears, from M. Thilorier's statement (*Ann. Ch. et Ph.*, LX. 427), to exceed even that of the gaseous acid, or of air. Thus from (0° to $+30$ Centigrade) 32° to 86° (Fahrenheit), its bulk increases from 20 to 29, which is four times greater than the dilatibility of air within the same range. It is insoluble in water and in the fat oils, but it is soluble in alcohol, ether, oil of turpentine, and carburet of sulphur.

A jet of liquid carbonic acid, emitted upon the bulb of a spirit thermometer, sinks it to -90° (Cent.), but the general frigorific effects do not correspond with this depression of temperature, in consequence of the almost entire want of conducting power in the gas, and its little capacity for heat. But as the case is different with regard to *vapors*, Thilorier tried the effect of a jet of liquid carbonic acid mixed with ether, and in this way he succeeded in producing a *cold blow-pipe*, which froze 50 grammes of mercury in a small glass capsule in a few seconds. Mr. Addams informs me that at common temperatures liquid carbonic acid acts with extreme slowness upon potassium and sodium, requiring a month to convert a piece of potassium, of the size of a pea, into carbonate of potassa: he observes that the potassium apparently derives its requisite equivalent of oxygen from the conversion of carbonic acid into carbonic oxide, inasmuch as no carbon is deposited when proper precautions have been taken to deprive the acid of water by fused chloride of calcium.

Solid Carbonic Acid. Thilorier first showed that carbonic acid may be obtained in a *solid* form by suffering a jet of the liquid acid to issue into a small phial, which immediately was lined by a white flocculent powder, consisting of the carbonic acid solidified or frozen by the intense cold resulting from its own expansion. When melted and resolidified, it appears clear and crystalline, like ice. It melts at -70° or -72° Fahrenheit, and the solid is heavier than the fluid. At this temperature it has a pressure of about 5.33 atmospheres. It is remarkable for the high tension of the vapor which it gives off whilst in the solid state: there is no other substance which at all comes near it in this respect, and it causes an inversion of what in all other cases is the natural order of events: thus, if as in the case with water, ether, mercury, or any other fluid, that temperature at which carbonic acid gives off vapor equal in elastic force to one atmosphere, be called its boiling point; or if (to produce the actual effect of ebullition) the carbonic acid be plunged below the surface of alcohol or ether, then we shall perceive that the freezing and boiling-points are inverted; that is, that the freezing-point is the hotter, and the boiling-point the colder of the two, the latter being about 50° below the former. (FARADAY.) In the solid state it moves about upon any polished surface, like a drop of water upon white-hot iron, and slowly disappears. Addams found the surfaces from which it had evaporated, in a negatively electrical state. In its usual state the flocculent acid feels like snow, and owing to its low conducting

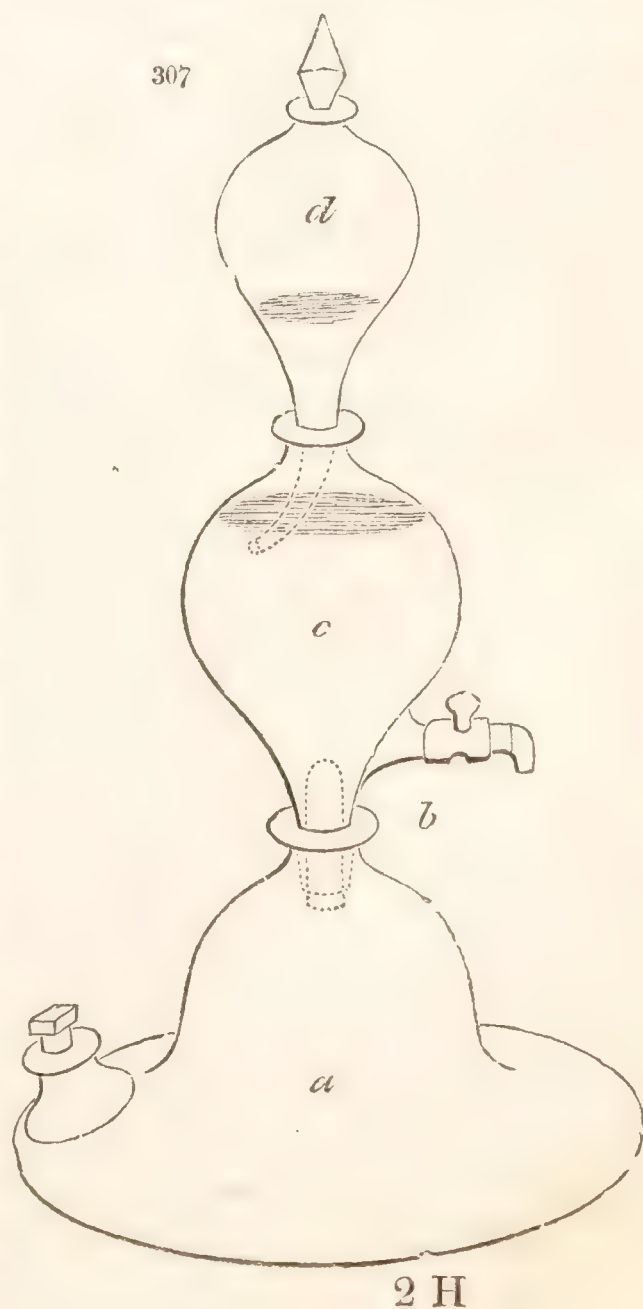
power it does not evaporate very rapidly nor feel extremely cold, though its actual temperature is lower than 100° below the 0° of Fahrenheit. When a little mercury is put into a saucer and covered by solid carbonic acid, the addition of a few drops of good ether forms a semifluid mass, by the contact of which the mercury is immediately frozen: in this way ten pounds of mercury may be frozen in less than eight minutes. In further illustration of the extraordinary relations of this substance, a large lump of the solid carbonic acid was kept, for a minute, in a red-hot crucible, and afterwards a pound of mercury was frozen with it. When a piece of the solid acid is put into a gas bottle, it gradually becomes gas, which may be collected as usual over water; or its conversion into the gaseous state may be more strikingly observed by letting up a small piece of it into an inverted jar of water. The following modification of this experiment I first saw performed by Professor Graham. A tall stoppered air-jar is inverted in the pneumatic trough, and half filled with oxygen; a piece of solid carbonic acid is then let up into it, by which the lower half of the jar soon becomes filled with very cold carbonic acid gas; if the glowing wick of a taper, attached to a long wire, be then plunged through the upper opening of the jar into the oxygen, it is instantly kindled into flame, but extinguished by causing it to descend into the inferior atmosphere of carbonic acid; and by a little care the wick may be left glowing, and then lifted into the oxygen, when it again bursts into flame: this alternate extinction and reproduction of flame may in this way be many times repeated.

Properties of Carbonic Acid Gas. This gas is colorless, of a slightly sour odor and taste, and much heavier than atmospheric air, its specific gravity being about 1.52. Compared with hydrogen its sp. gr. is as 22 to 1. 100 cubic inches weigh 47.2 grs. at mean temperature and pressure, (49.978 grains at 32° . THOMSON.) It is perfectly unrespirable, for on attempting to breathe it in a pure state the epiglottis is spasmodically closed, and no air entering the lungs, suffocation is the direct consequence. When so far diluted with air as to admit of being received into the lungs, it operates as a narcotic poison, producing drowsiness and insensibility, and this, even when a candle will burn in the mixture. (CHRISTISON.) Hence the danger of a confined room in which a pan of burning charcoal is placed. When the gas is respired in the lowest poisonous proportion, the symptoms come on very gradually, and the transition from life to death is usually tranquil; this is what we learn from the history of suicides. The symptoms in such cases appear closely to resemble those which indicate the progressive influence of opium, or any other narcotic poison on the body. The best means of resuscitation are the employment of cold affusion with stimulating applications to the chest and extremities: if the surface be cold a warm bath should be used. (A. TAYLOR, *Med. Jur.*, 550.) Butterflies, and other insects of which it is desired to preserve the colors unimpaired, may sometimes be conveniently suffocated by this gas. It immediately extinguishes the flame of a taper, and this even when considerably diluted with atmospheric air. In this way its weight may be conveniently shown by placing a lighted taper at the bottom of a tall glass jar, and then pouring the gas out of a dry bottle into it; it descends and extinguishes the flame, and will remain for some time in the lower part of the vessel. Like other gases, however,

notwithstanding its density, it soon blends with, and diffuses itself through, the mass of surrounding air. In wells, and in some caverns, carbonic acid frequently occupies the lower parts, while the upper parts are free from it. The miners call it *choak damp*. In these cases it issues from crevices in the earth, and is produced by unknown sources.

When water is agitated in carbonic acid, it takes up its own volume of the gas at common temperature and pressure, and acquires a slight increase of specific gravity (about 1.0018). Under increased pressure a much larger quantity is absorbed. It thus becomes brisk and tart, and reddens delicate vegetable blues. If litmus paper, thus reddened, be exposed to the air, the blue color returns as the acid evaporates; hence an easy distinction between the paper reddened by any of the more fixed acids, in which the change of color is permanent. In the same way, infusion of litmus thus reddened becomes blue when the carbonic acid is expelled by boiling. By freezing, boiling, or exposure to the vacuum of the air-pump, the gas is given off, and it gradually makes its escape when exposed to air, collecting in small bubbles upon the sides of the containing vessel, and passing off with especial rapidity when any foreign substances are thrown in, or when any substance is dissolved in the water; thus it is, that sugar added to soda-water, cyder, champagne, or other similar carbonated liquors, occasions in them an immediate and abundant effervescence.

Porter, ale, cyder, and many other beverages, derive their briskness from carbonic acid. The effervescent quality of many mineral waters is also referable to the presence of this gas, and they are often imitated by condensing carbonic acid into water, either by a condensing pump, or by *Nooth's apparatus*, as represented in the annexed wood-cut (fig. 307). It consists of three vessels, the lowest, *a*, flat and broad, so as to form a steady support; it contains the materials for evolving the gas, such as pieces of marble and dilute hydrochloric acid, of which fresh supplies may occasionally be introduced through the stopped aperture. The gas passes through the tube *b*, in which is a glass valve opening upwards, into the vessel *c*, containing the water or solution intended to be saturated with the gas, and which may occasionally be drawn off by the glass stop-cock. Into this dips the tube of the uppermost vessel *d*, which occasions some pressure on the gas in *c*, and also produces a circulation and agitation of the water. At the



top of *d* is a heavy conical stopper, which acts as an occasional valve, and keeps up a degree of pressure in the vessels.

The presence of carbonic acid is instantly detected by *lime water*, which it renders turbid, and causes a deposit of a white powder, which is *carbonate of lime*. The addition of water saturated with carbonic acid, to lime-water, also occasions a milkiness from the same cause. If excess, either of the gas or of its aqueous solution, be added to the lime-water, the precipitate is re-dissolved, carbonate of lime being soluble in water impregnated with carbonic acid. (See *Lime*.)

As all common combustibles, such as coal, wood, oil, wax, tallow, &c., contain carbon as one of their component parts, so the combustion of these bodies is always attended by the production of carbonic acid. It is also produced by respiration, hence it is detected, often in considerable proportion, in crowded and illuminated rooms, which are ill ventilated, and occasions difficulty of breathing, giddiness, and faintness. In the atmosphere it may also be detected, as has already been mentioned (page 371). Saussure found it in air from the summit of Mont Blanc; and Humboldt discovered it in air brought by Garnerin from a height of twenty thousand feet, to which he had ascended in a balloon. Its production in the lungs is easily shown, by blowing the expired air through lime-water by means of a small tube; it becomes milky, and soon deposits carbonate of lime. The quantity of carbonic acid ejected from the lungs at each ordinary expiration varies a little at different times of the day. (See *Respiration*.) According to Dr. Prout, it amounts on an average to 3.45 per cent. of the expired air, its limits being 3.3 and 4.1 per cent.

Carbonic acid is evolved from some of the *carbonates* by the simple operation of heat. Thus chalk, when heated, gives out carbonic acid, and becomes *quicklime*; but in these cases its escape is generally facilitated by the copresence of air or aqueous vapor; in other cases the carbonates may be heated to redness without the slightest tendency to the evolution of carbonic acid, as is the case with the carbonates of potassa and soda. Carbonic acid is also displaced by most of the other acids; and if dilute nitric, hydrochloric, or sulphuric acid be poured upon the carbonates, the presence of carbonic acid is indicated by *effervescence*.

Carbonic acid retards the putrefaction of animal substances: applied to the roots of vegetables in aqueous solution, it is generally propitious to their growth, as will be more fully shown in a future chapter. Most plants thrive in an atmosphere containing as much as a tenth or twelfth part of carbonic acid; and under certain circumstances, which will afterwards be explained, they decompose it, and evolve oxygen.

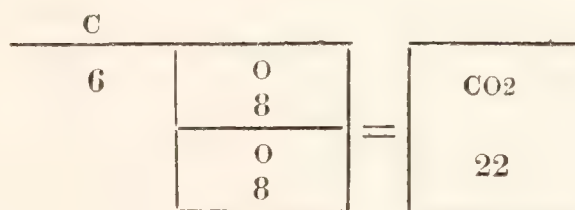
At high temperatures, carbonic acid is decomposed by several of the metals, and converted into carbonic oxide; and potassium and sodium, when sufficiently heated, burn in it, and are converted into potassa and soda, whilst the carbon of the gas is thrown down in the form of charcoal. There are some other substances which, at high temperatures, are capable of decomposing carbonic acid, and abstracting part of its oxygen; thus, if a mixture of 2 parts of hydrogen and 1 of carbonic acid by volume, be passed through a red-hot tube in the apparatus represented at p. 353, water is formed, and carbonic oxide passes into the receiver *d*, mixed with the excess of hydrogen. Dr. Henry also found that by passing a succession of electric sparks through carbonic acid confined over mercury,

a portion of it was resolved into carbonic oxide and oxygen. (*Phil. Trans.*, 1809, 448.) When the carbonic acid which escapes decomposition has been washed out by solution of potassa, an electric spark inflames the residuary mixture, the oxygen and carbonic oxide again uniting and reproducing carbonic acid.

Phosphorus, when heated in carbonic acid, does not decompose it; whence it might be inferred that carbon possessed a stronger affinity for oxygen than phosphorus; and such an inference is sanctioned by the decomposition of phosphoric acid, at high temperatures, by charcoal; but if complex attraction be brought into action, the case is altered, as was first shown by Tennant (*Phil. Trans.*, 1791, p. 182), and afterwards by Pearson (*Phil. Trans.*, 1792, p. 280). Thus it is, that certain carbonates are decomposed, at high temperatures, by phosphorus: if, for instance, the vapor of phosphorus be passed over ignited carbonate of lime, or carbonate of soda, charcoal is deposited, and phosphate of lime or phosphate of soda produced.

If carbonic acid be passed over red-hot charcoal, it becomes converted into carbonic oxide, by taking up an additional proportion of base. ($\text{CO}_2 + \text{C} = 2 \text{CO}$.) The blue flame, often seen upon the surface of a charcoal fire, arises from the combustion of the carbonic oxide formed in this way; the air entering at bottom, forms carbonic acid, which, passing through the red-hot charcoal, becomes converted into carbonic oxide. At a bright red-heat, iron and zinc decompose carbonic acid, by abstracting a portion of its oxygen, and forming oxide of iron or of zinc, and carbonic oxide, as already stated. Carbonic acid consists of

				Dumas and Stas.	Tennant.	Allen and Pepys.
Carbon.....	1	6	27.27	27.27	28.	28.6
Oxygen	2	16	72.73	72.73	72.	71.4
<hr/>						
Carbonic acid.....	1	22	100.00	100.00	100.	100.0
<hr/>						
	Vols.	Sp.Gr.			Vols.	Sp. Gr.
Carbon vapor	1	0.416	} = {	Carbonic oxide gas....	1.0	0.9706
Oxygen gas.....	1	1.109		Oxygen gas.....	0.5	0.5546
<hr/>						
Carbonic acid gas	1	1.525			1.0	1.5252



CARBONATES. The feeble affinity of carbonic acid for most of the bases has already been referred to, so that it is expelled from them by the greater number of the other acids with effervescence; the protocarbonates (constituted of 1 atom of base and 1 atom of acid) of ammonia, potassa, and soda, retain alkaline characters; they have an alkaline reaction upon vegetable colors, an alkaline taste, and form imperfect soaps with oil and water: they were therefore formerly termed *mild alkalis*, and *subcarbonates*. With the exception of the carbonates just mentioned, and of carbonate of lithia, these salts are decomposed at a red-heat under the influence of a current of air or aqueous vapor: with the same exceptions, the

basic and normal carbonates are insoluble in water, but the bicarbonates are soluble, and several of the insoluble neutral carbonates may be held in aqueous solution by excess of carbonic acid. The alkaline carbonates (and free carbonic acid, p. 466,) give a white precipitate which is soluble in hydrochloric acid, in baryta, strontia, and lime water. Baryta water is rendered slightly turbid by a solution of carbonate of soda, containing 1 part of the carbonate in from 70,000 to 80,000 of water. (GMELIN.)

CARBONIC ACID AND AMMONIA. CARBONATE OF AMMONIA. NH_3, CO_2 . When 1 volume of carbonic acid and 2 volumes of gaseous ammonia are mixed in a glass vessel over mercury, the gases are slowly condensed into a white solid, which lines the interior of the vessel. The same compound is deposited when a mixture of 1 volume of dry carbonic acid gas and 2 volumes of dry ammoniacal gas are passed through a cooled glass tube: it is strongly alkaline, smells of ammonia, and is volatile at 140° . It throws down carbonate of lime from a solution of chloride of calcium, without effervescence. If the gases be perfectly dry, they only condense each other in the above proportions, but if water be present, different compounds are obtained. This salt must obviously contain

					H. Rose.
Ammonia	1	17	43·6	44·69	
Carbonic acid	1	22	56·4	55·45	
<hr/>					
Carbonate of ammonia....	1	39	100·0	100·14	

If this salt be a true carbonate of ammonia it furnishes an exception in the general analogies of the ammoniacal salts of the oxyacids, inas-much as it is anhydrous: Dumas, therefore, regards it as a compound of amidogen, carbonic oxide, and water, and describes it under the name of *carbamide*: $\text{NH}_3, \text{CO}_2 = \text{NH}_2, \text{CO}, \text{HO}$; in this view of its constitution it is isomeric with hydrated urea.

SESQUICARBONATE OF AMMONIA. $2\text{NH}_3, 3\text{CO}_2, 2\text{HO}$. The carbonate of ammonia of commerce, when carefully prepared, appears to be this salt, though from the volatility of its components it frequently exhibits slight variations in its composition. It is generally met with in translu-cent cakes of a fibrous fracture, as obtained by sublimation from a mix-ture of carbonate of lime and sulphate or hydrochlorate of ammonia. When carbonate of lime and sulphate of ammonia are used for its pro-duction, the results are sulphate of lime, hydrated sesquicarbonate of ammonia, and free ammonia and water. $3 [\text{CaO}, \text{CO}_2] + 3 [\text{NH}_3, \text{SO}_3, \text{HO}] = 3 [\text{CaO}, \text{SO}_3] + [2\text{NH}_3, 3\text{CO}_2, 2\text{HO}] + \text{NH}_3, \text{HO}$: or, in reference to the oxide of ammonium theory, the equation will stand thus: $3 [\text{CaO}, \text{CO}_3] + 3 [\text{NH}_4\text{O}, \text{SO}_3] = 3 [\text{CaO}, \text{SO}_3] + [2\text{NH}_4\text{O}, 3\text{CO}_2] + \text{NH}_4\text{O}$. When sal-ammoniac is substituted for the sulphate, we have $3 [\text{CaO}, \text{CO}_2] + 3 [\text{NH}_3, \text{HCl}] = 3 \text{CaCl} + [2\text{NH}_3, 3\text{CO}_2, 2\text{HO}] + \text{NH}_3, \text{HO}$. The components, then, of this form of carbonate of ammonia are

										H. Rose. J. Davy.			
Ammonia	2	34	28·81	28·66	27·39	} = {	Oxide of ammo-		}	2	52	44·07	
Carbonic acid	3	66	55·93	50·55	54·58		nium			3	66	55·93	
Water	2	18	15·26	20·79	18·03		Carbonic acid						
<hr/>												<hr/>	
Sesquicarbonate	}	1	118	100·00	100·00	}			}	1	118	100·00	
of ammonia													

This salt has a pungent odor, a hot and saline taste, and powerful alkaline reaction: it is used in medicine as a stimulant and antacid, and is a useful source of other ammoniacal salts. It is obtained in an impure state by the destructive distillation of many azotised animal substances, constituting *salt of hartshorn*, and *smelling-salts*, the former contaminated by empyreumatic oil, the latter generally perfumed. Four parts of water at 60° dissolve about 1 of this salt, forming the *liquor ammoniæ sesquicarbonatis* of the *Pharmacopœia*. According to Scanlan, when a small quantity of water is poured upon it, the effect is to resolve it into carbonate and bicarbonate, hence it has by some been considered as $= [\text{NH}_3, \text{CO}_2 + \text{HO}, \text{CO}_2 + \text{NH}_4\text{O}, \text{CO}_2]$. When exposed to air, especially in the state of powder, it effloresces into bicarbonate of ammonia, and carbonate of ammonia volatilises. When its aqueous solution is heated, carbonic acid and a little ammonia is evolved, and the single carbonate remains dissolved. Boiled with alcohol or ether carbonic acid escapes, and a hydrated carbonate sublimes $= 2 \text{NH}_3, 2 \text{CO}_2, \text{HO}$. (H. ROSE.)

BICARBONATE OF AMMONIA, $(\text{NH}_3, 2\text{CO}_2, 2\text{HO})$ or, according to Graham's view $[\text{HO}, \text{CO}_2 + \text{NH}_4\text{O}, \text{CO}_2]$, is the residue of the preceding salt after exposure to air: it also crystallizes out of a solution of the sesquisalt saturated with carbonic acid gas. It forms the precipitate produced by the addition of alcohol to the solution of the sesquicarbonate, (J. DAVY,) and is sometimes formed during the sublimation of the carbonate upon the large scale. (R. PHILLIPS, *Ann. Phil.*, xvii. 110.) Its crystals are isomorphous with those of bicarbonate of potassa. It is nearly inodorous and tasteless; has a slight alkaline reaction; and evaporates on exposure to air, especially if damp, in which case carbonic acid is set free and the vapor is alkaline: it is soluble in about 6 parts of water at 55° . At the temperature of 100° its solution gives off carbonic acid rapidly, and becomes alkaline. It is insoluble in alcohol, but when covered by alcohol and exposed to air, carbonic acid escapes, and a solution of the single carbonate is formed. Its components are

				J. Davy.	R. Phillips.	H. Rose.
Ammonia	1	17	21.52	21.56	21 16	21.60
Carbonic acid.....	2	44	55.69	56.01	55.50	55.88
Water	2	18	22.79	22.43	23.34	22.52
<hr/>						
Bicarbonate of } ammonia.....	1	79	100.00	100.00	100.00	100.00

Several other definite hydrated carbonates of ammonia have been described by H. Rose. (*Poggend.*, XLVI. 352, and *Scientific Memoirs*, ii. 98.) One of these is obtained by pouring upon the sesquisalt a sufficiency of boiling water to dissolve it, and immediately closing it up in a strong bottle so as to prevent the escape of carbonic acid: as it cools, large prismatic crystals are formed, containing

					H. Rose.
Ammonia	2	34	20.36		20.02
Carbonic acid	4	88	52.70		52.89
Water	5	45	26.94		27.09
<hr/>					
	1	167	100.00		100.00

CARBON AND CHLORINE. CHLORIDES OF CARBON. For the discovery of the compounds of carbon with chlorine we are indebted to Faraday

(*Phil. Trans.*, 1821, p. 47). The circumstances under which they combine were subsequently investigated by Regnault (*Ann. Ch. et Ph.*, Lxix. 151, and Lxx. 104), and by Dumas (*Ann. Ch. et Ph.*, Lxxiii. 95). There are four chlorides of carbon, namely, a dichloride = C_2Cl ; a chloride = CCl ; a sesquichloride = C_2Cl_3 , and a bichloride = CCl_2 . Some other combinations of chlorine and carbon have also been indicated, arising out of the decomposition of organic compounds, and which will be adverted to hereafter.

DICHLORIDE OF CARBON. BICARBURET OF CHLORINE. C_2Cl . This compound was originally obtained in Sweden, whence it was brought by Julin, and submitted to analysis by Phillips and Faraday. It appears to have been accidentally formed in distilling nitric acid from a mixture of sulphate of iron and nitre, both salts having been impure. (*Ann. of Phil.*, N. S., i. 216, and ii. 150.) Regnault obtained it by repeatedly passing the vapor of the protochloride through a porcelain tube filled with fragments of porcelain, at a high red-heat: it was deposited in crystals in the cooler part of the tube and purified by solution in ether, and evaporation. When gently heated it rises in vapor without decomposition, and yields a crystalline sublimate. It is insoluble in water, but soluble in alcohol, ether, and essential oils. It sinks in water. It burns with a red flame, giving off much smoke and fumes of hydrochloric acid. Acids do not act on it. When its vapor is highly heated in a tube, chlorine is given off, and charcoal deposited: when potassium is burnt in it, it forms chloride of potassium and liberates charcoal: when it is detonated over mercury, with oxygen, carbonic acid and chloride of mercury are the results: passed over hot oxide of copper, it forms chloride of copper and carbonic acid; and over hot lime, it occasions ignition, and produces chloride of calcium and carbonic acid. The results of its analysis by oxide of copper, show that it consists of

Carbon.....	2	12	25
Chlorine	1	36	75
<hr/>					
Dichloride of carbon	1		48		100

PROTOCHLORIDE OF CARBON. CCl . When *sesquichloride of carbon* is passed through a red-hot tube containing fragments of rock-crystal to increase the heated surface, it gives off a portion of chlorine, and is converted into a liquid *protochloride of carbon*. Regnault obtains this protochloride by dissolving the sesquichloride in alcohol, and then dropping into it an alcoholic solution of hydrosulphuret of potassium so long as sulphuretted hydrogen is evolved: chloride of potassium falls, and the clear solution, poured off and distilled from the excess of hydrosulphuret, is mixed with water: the chloride of carbon separates in the form of a heavy colorless liquid. Its specific gravity is 1.6: it is not combustible, except retained in the flame of the spirit-lamp, when it burns with a yellow flame, much smoke, and the fumes of hydrochloric acid. It does not congeal at 0° ; it boils at about 165° , (FARADAY); 250° , (REGNAULT), the density of its vapor being 5.82. (Berzelius supposes that Faraday and Regnault describe isomeric varieties of the same chloride.) It is insoluble in water, but soluble in alcohol, ether, and the oils. It is not affected by the acids or alkalis, nor, at common temperatures, by solu-

tions of silver. It dissolves chlorine, iodine, sulphur and phosphorus. It consists of

Carbon.....	1	6	14.3
Chlorine	1	36	85.7
<hr/>					
Protochloride of carbon	1		42		100.0

SESQUICHLORIDE OF CARBON. C_2Cl_3 . By exposing the variety of carburetted hydrogen usually termed *olefiant gas*, mixed with great excess of chlorine to the action of light, a white crystalline substance is obtained, which, when purified by washing with water, is a *sesquichloride of carbon*. It is formed as follows: A glass vessel capable of holding about 200 cubic inches, is properly mounted with a stop-cock, and exhausted upon the air-pump: it is then nearly filled with chlorine, and afterwards placed in connexion with a jar of olefiant gas standing over water, and, as much as can enter having passed in, the cocks are shut, and the whole left for a short time: when the fluid compound of chlorine and carburetted hydrogen (described further on) has formed, the cocks are re-opened, and a fresh portion of carburetted hydrogen rushes in, in consequence of the condensation which has taken place; this is left, as before, to combine with the remaining chlorine, and the process continued, until no further action ensues, and the vessel is, in fact, full of carburetted hydrogen: chlorine is then similarly admitted, in repeated portions, and, ultimately, a quantity of the liquid hydrochloride of carbon is obtained, with an atmosphere of chlorine above it: in this state it is exposed to the direct rays of the sun. The chlorine speedily disappears, and hydrochloric acid is formed: this is absorbed by the admission of a little water; another atmosphere of chlorine is then admitted, and exposure to the sun repeated; by continuing these operations, the whole of the hydrogen is at length abstracted in the form of hydrochloric acid, and crystals are formed in the liquid; these are to be collected, washed, and pressed between bibulous papers, then introduced into a glass tube, and sublimed by a spirit-lamp; the pure substance, with water, will rise at first, but the last portions will be partially decomposed, hydrochloric acid will be liberated, and charcoal left. The sublimed portion is then to be dissolved in alcohol, and poured into a weak solution of potassa, by which the substance is thrown down, and the hydrochloric acid neutralized and separated; then wash the substance with repeated affusions of water, collect and dry it, first between folds of paper, and then in the exhausted receiver of the air-pump. If quite pure, it sublimes without any change, and a small portion dissolved in ether gives no precipitate with nitrate of silver.

In this state it is nearly tasteless; its odor resembles camphor; its specific gravity is about 2; it is a non-conductor of electricity, and powerfully refracts light. It is volatile, and in close vessels fuses at 320° ; it boils at 360° , and may be distilled without decomposition: its vapor again condenses in crystals as it cools. According to Regnault, the density of its vapor is 8.157, or 120 in reference to hydrogen = 1. It is not very combustible, but burns when held in the flame of a spirit-lamp, with the emission of much smoke and acid fumes. It burns vividly in oxygen gas. It is insoluble in water, but readily soluble in alcohol and

ether; these solutions deposit arborescent and quadrangular crystals. It also dissolves in volatile and fixed oils. It is scarcely acted upon by alkaline and acid solutions, but most of the metals decompose it at a red heat. Potassium burns brilliantly in its vapor, causing the deposition of carbon, and the production of chloride of potassium. The metallic oxides also decompose it at high temperatures, producing metallic chlorides, and carbonic acid or oxide, according to the proportion of oxygen present; no water is produced, showing the absence of hydrogen in the compound. It appears, from various analytical experiments upon this compound, among which may be mentioned its decomposition by passing it through red-hot peroxide of copper, that it is a *sesquichloride of carbon*, consisting, therefore, of

Carbon	2	12	10
Chlorine	3	108	90
<hr/>					
Sesquichloride of carbon.....	1		120		100

BICHLORIDE OF CARBON. CCl_2 . This compound may be obtained by the action of chlorine and light on that variety of carburetted hydrogen known as marsh-gas or fire-damp. (See *Bihydroguret of Carbon*, p. 476.) It may also be obtained by the action of chlorine on hydrochloric ether, or on chloroform, compounds described under the head of *ethers*, and amongst organic products; but the best process for procuring it is that of Kolbe. (BERZELIUS, *Lehrbuch*, i. 303, Ed. 1843.) A mixture of chlorine and the vapor of sulphuret of carbon is passed through a porcelain tube filled with fragments of porcelain, and at a high red-heat: chloride of sulphur and bichloride of carbon are formed, which produce a deep reddish-yellow liquid, condensable in a well-cooled receiver: the chlorine is best saturated with the vapor by merely passing it through a flask containing sulphuret of carbon, which is sufficiently volatile to be carried off in adequate quantity with the current of chlorine; the flask should not be heated, as in that case the excess of the vapor is wasted. The red liquid is left for some time in contact of and occasionally shaken with a strong solution of caustic potassa, which absorbs the chloride of sulphur, so that the bichloride of carbon may be distilled off from the mixture.

Bichloride of carbon is a colorless liquid of a peculiar aromatic but acrid and suffocating odor: its sp. gr. is 1.59; it boils at 172° : the density of its vapor being 5.3. (REGNAULT.) It is insoluble in water, but soluble in alcohol and ether: it is not decomposed by caustic or sulphuretted alkalis: passed through a red-hot porcelain tube, more or less chlorine is separated, and one or other of the preceding chlorides formed. It consists of

						Regnault.
Carbon	1	6	7.69 7.82
Chlorine	2	72	92.31 92.18
<hr/>						<hr/>
Bichloride of carbon.....	1		78		100.00	100.00

CARBON AND IODINE. PROTIODIDE OF CARBON. CI . This compound is prepared by triturating together equal parts of dry sesquiodide of carbon and perchloride of phosphorus, and gently heating the mixture in a tubulated retort, the beak of which dips into water; a liquid passes over,

which falls to the bottom of the water, and which, when carefully separated and mixed with four or five parts of sulphuric acid, is thus freed from hydrochloride of carbon, and remains at the bottom of the acid; it is ultimately separated, and having been washed with a solution of potassa, and lastly with water, is the pure *iodide of carbon*. It is a heavy, yellow liquid, of a peculiar etherial odor and sweet taste; very little soluble in water, and not congealed at 32° . Exposed to air it gradually reddens. It does not act upon potassium; in the flame of a candle it gives out iodine. It is decomposed at a red heat when passed over peroxide of copper, and from the produced carbonic acid, Serullas inferred (*Ann. Ch. et Ph.*, xxxix. 231) that it consists of

Carbon.....	1	6	4.58
Iodine	1	126	95.42
<hr/>					
Protiodide of carbon	1		132		100.00

SESQUIODIDE OF CARBON. C_2I_3 . This compound of carbon and iodine was first obtained by Serullas, and considered as a hydriodide of carbon. (*Ann. Ch. et Ph.*, xx. 163, and xxii. 172.) It was subsequently examined by Mitscherlich. (*Ann. Ch. et Ph.*, xxvii. 85.) It is produced in the form of a yellow precipitate, when a saturated solution of iodine in alcohol is mixed with a strong alcoholic solution of potassa or soda: part of the iodine combines with the potassium or sodium; and the liberated oxygen unites to the hydrogen of the alcohol to form water, whilst another part of the iodine combines with the carbon of the alcohol. Iodide of carbon is of a lemon-yellow color, and a sweetish taste. It crystallizes in brilliant spangles; its smell somewhat resembles that of saffron: its specific gravity is nearly 2. It is not sensibly soluble in water, but dissolves in 80 times its weight of alcohol of 0.825 specific gravity at 60° , and in 25 times at 95° . One part dissolves in 7 of ether. It also dissolves in fat and volatile oils; and when its solution in oil of lemon-peel is exposed to light, it is decomposed, and charcoal and iodine are deposited. Sulphuric, sulphurous, nitric, and hydrochloric acids have no action upon it, nor has aqueous solution of chlorine; but gaseous chlorine decomposes it, and forms chloride of iodine, and a white substance, which is probably a chloride of carbon. At common temperatures it gradually evaporates when exposed to air, and at 212° volatilizes without decomposition; between 240° and 248° it enters into fusion, and is soon decomposed, giving rise to vapors of iodine and a brilliant charcoal. If moisture be present, carbonic and hydriodic acids may be formed. Serullas analyzed this compound by passing it over ignited peroxide of copper. (*Ann. Ch. et Ph.*, xxxix. 230.) It appears to be a *sesquiodide*, and to consist of

Carbon.....	2	12	3.07
Iodine	3	378	96.93
<hr/>					
Sesquiodide of carbon....	1		390		100.00

CARBON AND BROMINE. PROTOBROMIDE OF CARBON. CBr . Löwig obtains this compound by gradually adding bromine to alcohol (sp. gr. .833) as long as it is dissolved, when hydrobromic acid is evolved with effervescence; alcoholic solution of potassa is then added till the mixture becomes colorless, and then heat is applied to expel the greater part of

the alcohol: on the addition of water, camphor-like crystals of protobromide of carbon are gradually formed, and, at the same time, an oil-like liquid (sesquibromide?). By the protracted action of bromine on ether, and subsequent distillation, hydrobromic acid passes off together with a colorless oily liquid, and on saturating the sour residue with solution of potassa, crystals of the protobromide are also deposited. This substance forms white fatty scales; it has an ethereal odor, and a pungent bitterish taste. It fuses at about 122° , and its vapor condenses in acicular crystals. It is heavier than, and insoluble in, water; soluble in alcohol and ether; is not decomposed by acids or alkalis, and is without action on nitrate of silver. (BERZELIUS, *Lehrbuch*.) It consists of

						Löwig.
Carbon	1	6	7.14 7.3
Bromine	1	78	92.86 92.7
<hr/>						<hr/>
Protobromide of carbon	1		84		100.00	100.0

SESQUIBROMIDE OF CARBON. C_2Br_3 ? This compound, discovered by Serullas (*Ann. Ch. et Ph.*, xxxiv. and xxxix.), is formed by adding two parts of bromine to one of the solid iodide of carbon, and just enough solution of potassa to occasion the disappearance of the free iodine. A liquid bromide of carbon will appear at the bottom of the solution, which is to be separated by a funnel or otherwise, but without washing with water, and allowed to stand till it has become quite clear; during this time, crystals of iodate of potassa form upon the surface; the clear fluid beneath is to be withdrawn, and put into a weak solution of potassa, for the purpose of decomposing a little protiodide of carbon formed at the same time: a little bromide is also decomposed, but that which remains is soon left in a pure state. The principal properties of this, (which is probably a *sesquibromide of carbon*,) and the differences between it and the liquid protiodide, are as follows: the bromide becomes solid, hard, and crystalline, at 32° , and remains solid up to 43° ; the iodide remains fluid in the lowest temperatures. The bromide gives red vapor; the iodide violet vapor, when heated in the flame of a spirit-lamp. Neither of them act upon water, but are slowly decomposed in weak alkaline solutions. This compound, like the iodide, is by some suspected to contain hydrogen.

FLUORIDE OF CARBON is unknown.

CARBON AND HYDROGEN. These elements unite in several proportions, forming gaseous, liquid, and solid compounds, among which it is sometimes difficult to distinguish those which ought to be considered as distinct and definite from others which are mere mixtures. These compounds are generally termed *hydrocarbons*, or *hydrocarburets*, and amongst them are some striking illustrations of one species of *isomerism* (from *ισος*, *equal*, and *μερος*, *part*), that is, of compounds differing, often essentially, in their physical or chemical properties, or both, and yet apparently produced by the union of the same elements bearing the same ratio to each other. Bihydrocarbon or olefiant gas, and quadrihydrocarbon or etherine, for instance, are in this predicament; when analyzed they are each found to consist of carbon, and hydrogen, in the same relative proportions, namely, 1 atom of carbon united to 1 atom

of hydrogen; but the density of a volume of the former is to that of the latter, as 1 to 2; hence there are twice the number of simple atoms in an equivalent of etherine, that exist in an equivalent of olefiant gas; and assuming the density of hydrogen as = 1, that of olefiant gas is 14, and of etherine 28; hence we consider an atom of olefiant gas as constituted of 2 atoms of carbon, and 2 atoms of hydrogen, C_2H_2 , and an atom of etherine as constituted of 4 atoms of carbon, and 4 atoms of hydrogen, C_4H_4 . Their respective volumes, equivalents, and densities, may, therefore, be represented thus; as will be obvious by referring to the following more detailed state-

Hydrogen.	Olefiant.	Etherine.
1	14	28

ment of their composition. Here, therefore, although the compounds are isomeric, they are represented by different equivalent numbers; but there are cases of *isomerism* in which the same elements are united in the same ratio, so as to produce compounds represented by the same equivalent number, yet essentially distinct in their chemical characters. Urea, for instance, has the *empyric* formula $C_2H_4O_2N_2$; it is a basic body; but the same elements constitute hydrated cyanate of ammonia, in which case they may be arranged under two rational formulæ; namely, as NH_3, C_2NO, HO , representing ammonia, cyanic acid, and water; or, NH_4O, C_2NO , which represents oxide of ammonium and cyanic acid. The equivalent is here the same in all, namely, 60. To these cases the distinctive terms *polymeric* and *metameric*, have sometimes been applied. In combining the elements, in cases of this kind, into rational formulæ, we must be guided by experiment, or analogy, or both: so in regard to the preceding formulæ for cyanate of ammonia, that which represents it as a cyanate of oxide of ammonium is sanctioned by the results of electrolysis. To give a similar case of an inorganic salt, sulphate of potassa is empirically represented by KSO_4 ; rationally, by KO, SO_3 , or by K, SO_4 , and the latter is probably the more correct statement of its proximate composition. In purely inorganic compounds, the elements seem to adhere to one form of arrangement, for in them, cases of true isomerism never perhaps occur, the elements K, S, O_4 always forming the same salt; but it is possible that a body having very different properties might result either from other modes of their atomic arrangement, or by doubling the number of their atoms: in which case, if we assume K, SO_4 to be the rational formula of the salt usually called sulphate of potassa, then, either KO, SO_3 , or KO_2, SO_2 , or $2 [KSO_4]$, &c., might possibly form compounds of perfectly distinct properties.

Carbon and hydrogen form a numerous and important series of compounds, many of which are isomeric, and many exclusively of organic origin, that is, not admitting of artificial production. It must also be recollected, that the principal elements of the infinitely varied products of organization are carbon, hydrogen, oxygen, and nitrogen, so that considerable difficulty attends the arrangement and classification of these compounds, and by far the greater number must necessarily be referred to the chemistry of organic bodies. Some writers have consigned the entire history of carbon and its combinations to "Organic Chemistry;" others have separated the carboniferous compounds into those which are common to the three kingdoms of nature, and those which are peculiar

to vegetables or animals; and others have adopted an arrangement having reference merely to convenience and perspicuity: the latter, under existing circumstances, seems the preferable plan, and I shall proceed in this place to describe such of these compounds as admit of artificial production, and more especially those which are either binary, or binary derivations, or which require description in reference to the history of metallic compounds.

LIGHT CARBURETTED HYDROGEN. BIHYDROURET OF CARBON. FIRE-DAMP OF COAL MINES. MARSH GAS. CH_2 . Under these names an important variety of hydrocarbon is designated, which occasionally occurs pent up in cavities in coal-mines (DAVY, *Phil. Trans.*, 1815,) and which is also said to be abundantly formed in stagnant pools during the spontaneous decomposition of vegetable matter, and to be procured by stirring up the fetid mud, and collecting the gas that rises in an inverted glass jar; in this state it is mixed with a little nitrogen and with carbonic acid; the latter may be separated by washing the gas in lime-water or in a solution of caustic potassa. The gas procured from a *blower* in a coal-mine, after having been washed with lime-water, furnishes this compound in a pure state; but it may be best obtained by the decomposition of certain *acetates*, under the following conditions, first pointed out by Persoz, and described by Dumas, (*Sur les Types Chimiques, Ann. Ch. et Ph.*, LXXII. 73;) 40 parts of crystallized acetate of soda, 40 of caustic potassa, and 60 of powdered quick-lime are well mixed and heated in a glass retort, the use of the lime being to prevent the action of the alkali upon the glass; at a heat approaching dull redness, the gas is abundantly evolved and may be collected over water: the action is determined by the affinity of the alkaline bases for carbonic acid and the instability of the acetic acid, at high temperatures; an atom of acetic acid and an atom of water producing carbonic acid, which combines with the soda and potassa, and light carburetted hydrogen which passes off; ($\text{C}_4\text{H}_3\text{O}_3 + \text{HO}$), yielding 2CO_2 , and 2CH_2 . A mixture of 1 equivalent of fused hydrate of baryta (= 86 parts) and 1 of anhydrous acetate of soda (= 83 parts) similarly treated, also yield a pure gas.

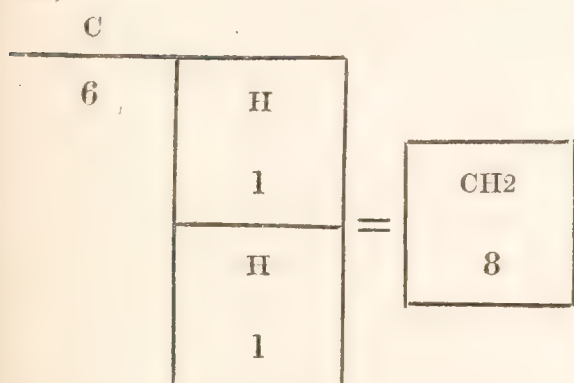
Sir H. Davy found the specific gravity of this gas to be 0.555, and compared with hydrogen as 8 to 1. 100 cubical inches weigh 17.4 grains (or, according to Thomson, 18.2148 grains at the temperature of 32°), and nearly the same specific gravity is assigned to this gas (0.559) by Henry and Dalton. Its refractive power is 2.097, air being 1.000. When pure, it is of course unrespirable, but it is not very noxious when mixed with air. It is sparingly soluble in water, 14 cubic inches of which take up about 1 of the gas. It is hardly sensibly soluble in alcohol or ether, and in oil of turpentine the proportion dissolved is not probably one-fifteenth of the volume of the fluid employed. (FARADAY.) It is inflammable, burning with a yellow flame, and producing carbonic acid and water; it has, when quite pure, scarcely any odor. Its specific heat has not been determined. It is not decomposed by electric sparks; but when passed through a white-hot tube, deposits a portion of its carbon. When chlorine is mixed with the gas of the acetates, there is no immediate action; but when 1 volume of the gas and 3 of chlorine are mixed and exposed to diffuse light, a violent explosion soon ensues,

breaking the vessels and depositing carbon. When the gas is previously mixed with its volume of carbonic acid, the chlorine may be added without danger, and an oily liquid is deposited, which is chiefly chloride of carbon. This result is best obtained by connecting a flask, holding about a quart measure of the carburetted hydrogen, with one of thrice that capacity of chlorine, by means of a tube of small bore, and so placing them that the chlorine may be below and the carburetted hydrogen above: under the influence of the sun's rays, the gases thus gradually mix and react on each other, producing the oily liquid, which, when collected and dried, yielded C 7·5, H 0·1, Cl 92·4 *per cent.*: assuming the trace of hydrogen as accidental, the proportions of carbon and chlorine are nearly as 6 to 72, or = CCl_2 , giving therefore the bichloride of carbon. When this gas is passed with chlorine through a red-hot tube, carbon is thrown down and hydrochloric acid formed.

100 volumes of this gas require 200 of oxygen for perfect combustion, and the result is *water*, and 100 volumes of *carbonic acid*. 100 volumes of carbonic acid contain 100 of oxygen, or half the quantity consumed; the remaining 100 volumes, therefore, must have combined with 200 of hydrogen to form water; hence this gas is constituted of

Carbon.....	1	6	75
Hydrogen	2	2	25
<hr/>					
Light Carb. Hydrogen	1		8		100

Or,



Sir H. Davy made several experiments on the combustibility and explosive nature of this gas. He found that when 1 volume was mixed with 1 of air, they burnt by the approach of a lighted taper, but did not explode; 2 of air and 3 of air to 1 of gas produced similar results. When 4 of air and 1 of the gas were exposed to a lighted candle,

the mixture being in the quantity of 6 or 7 cubical inches in a narrow-necked bottle, a flame descended through the mixture, but there was no noise: 1 volume of gas inflamed with 6 of air in a similar bottle, produced a slight whistling sound: 1 of gas with 8 of air, rather a louder sound: 1 with 10, 11, 12, 13, and 14, still inflamed, but the violence of combustion diminished. In 1 of gas and 15 of air, the candle burnt, without explosion, with a greatly enlarged flame; and the effect of enlarging the flame, but in a gradually diminishing ratio, was produced as far as 30 parts of air to 1 of gas. The mixture which seemed to possess the greatest explosive power was that of 7 or 8 volumes of air to 1 of gas; but the report produced by 50 cubical inches of this mixture was less than that produced by one-tenth of the quantity of a mixture of 2 parts of atmospheric air and 1 of hydrogen.

In reference to the *degree of heat* required to explode this gas mixed with its proper proportion of air, it was found that a common electrical spark would not explode 5 parts of air and 1 of the gas, though it exploded 6 parts of air and 1 of the gas; but very strong sparks from the discharge of a Leyden jar seemed to have the same power of exploding

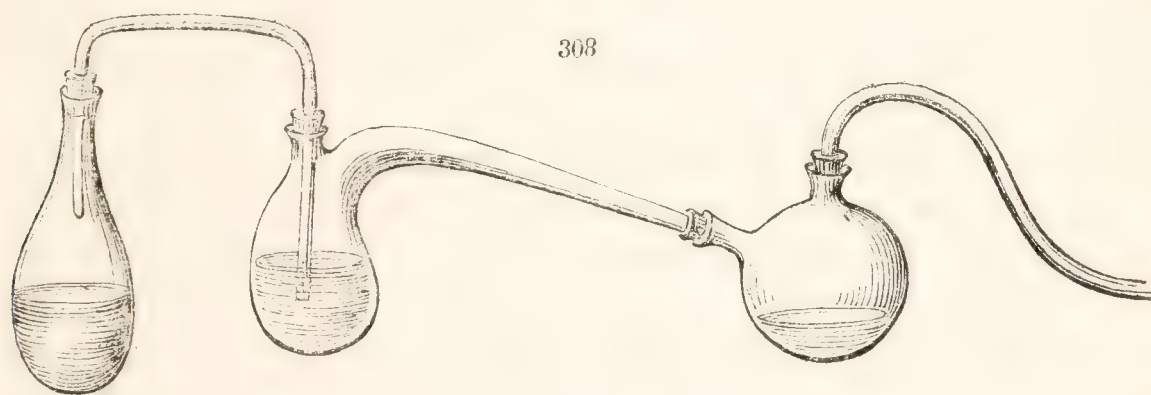
different mixtures of the gas as the flame of the taper. Well-burned charcoal, ignited to the strongest red-heat, did not explode any mixture of air and of the fire-damp; and a fire made of well-burned charcoal, *i. e.* charcoal that burned without flame, was blown up to whiteness by an explosive mixture containing the fire-damp, without producing its inflammation. An iron-rod at the highest degree of red-heat, and at the common degree of white-heat, did not inflame explosive mixtures of the fire-damp; but, when in brilliant combustion, it produced the effect. The flame of gaseous oxide of carbon, as well as that of olefiant gas, exploded the mixtures of the fire-damp.

In respect of combustibility, then, this hydrocarburet differs materially from the other common inflammable gases. Sir Humphry found that olefiant gas, which explodes mixed in the same proportion with air, is fired by both charcoal and iron heated to redness. Carbonic oxide, which explodes when mixed with 2 parts of air, is likewise inflammable by red-hot iron and charcoal; and hydrogen, which explodes when mixed with three-sevenths of its volume of air, takes fire at the lowest visible heat of iron and charcoal; and the case is the same with sulphuretted hydrogen. When 6 of air and 1 of the hydrocarburet were exploded over water by a strong electrical spark, the explosion was not very strong, and, at the moment of the greatest expansion, the volume of the gas did not appear to be increased more than one-half. (This appears the expansion when the tube is very small; in larger tubes it is considerably more. The volume of the gas appears at least tripled during the explosion.) Nitrogen and carbonic acid mixed in different quantities with explosive mixtures of fire-damp, diminished the velocity of the inflammation. Nitrogen, when mixed in the proportion of 1 measure to 6 of an explosive mixture containing 12 of air and 1 of fire-damp, deprived it of its power of explosion; when 1 measure of nitrogen was mixed with 7 of an explosive mixture, only a feeble blue flame slowly passed through it. One volume of carbonic acid to 7 of an explosive mixture, deprived it of the power of exploding; so that its effects are more remarkable than those of nitrogen: probably, in consequence of its greater capacity for heat, and perhaps, likewise, of a higher conducting power connected with its greater density. These inquiries are important, in reference to the existence of this variety of hydrocarburet, under the name of *fire-damp*, in coal-mines.

OLEFIANT GAS. ELAYLE. CARBURET OF HYDROGEN. BIHYDROCARBON. C_2H_2 . This gas was discovered in 1796, by the associated Dutch chemists, Bondt, Dieman, Van Troostwick, and Lawerenburg. (*Journ. de Phys.*, xiv. 178; *Ann. de Chim.*, xxi. 48.)

It is usually obtained by the decomposition of alcohol by sulphuric acid. For this purpose about two parts of the acid and 1 of alcohol (by measure) are put into a retort, and heated by a lamp; complicated changes ensue, which will be more fully explained under the article *Alcohol*, and soon after the mixture boils, the gas is evolved. It may be collected over water, and should be well washed with lime water, or with solution of potassa, to abstract sulphurous and carbonic acids; it also retains a little ethereal vapor, which may be removed by agitating it with weak alcohol and afterwards with water. A more refined process for the production of olefiant gas consists in passing the vapor of hydrous alcohol

into sulphuric acid so far diluted as to have its boiling point reduced to 325° , (about 2 parts of oil of vitriol, sp. gr. 1.8, and 1 of water.) The acid is put into a tubulated retort, to which a tubulated receiver and gas tube are annexed, and the alcohol (sp. gr. 0.850) is introduced into a flask from which a bent tube passes through the tubulure of the retort, so as to convey the alcoholic vapor into the boiling acid (fig. 308): there should also be a thermometer in the acid, and when this indicates the temperature of about 325° , heat is applied to the alcohol flask, so as to send its vapor through the boiling acid at such a rate as to maintain as nearly as possible the above temperature. Under these circumstances the vapor of the hydrated alcohol is converted (catalytically?) into olefiant gas and aqueous vapor: the latter, with a little alcohol and ether, passes into the receiver, which should be well cooled, and the olefiant gas goes off by the bent gas tube, and may be collected as usual; when the process is properly conducted, the acid is not discolored, and no sulphurous acid is formed. (MITSCHERLICH.)



The specific gravity of olefiant gas, as usually prepared, is about .980, or compared with hydrogen as 14 to 1, and 100 cubical inches weigh about 30 grains. According to Thomson, its specific gravity is 0.9722 (the same as that of nitrogen and of carbonic oxide), and 100 cubic inches at the temperature of 32° weigh 31.8790 grains. Its refractive power is 1.818 air, being $=1.000$: and its specific heat compared with that of air, is 1.53 (DULONG), 1.55 (DE LA ROCHE and BERARD), being greater than that of any other gas.

Under the combined influence of intense cold and pressure, Faraday (*Phil. Trans.*, 1845, p. 160), succeeded in condensing olefiant gas into a clear colorless transparent liquid, not solidifiable; its vapor exerts a pressure of 26.9 atmospheres at 0° .

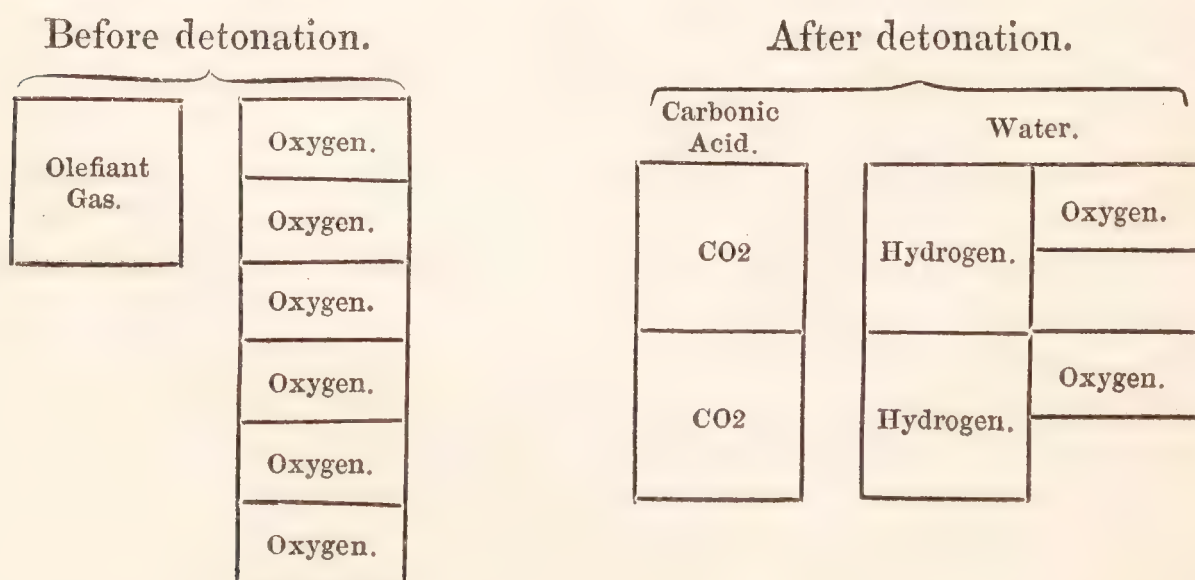
Olefiant gas, when carefully purified, has little odor, though it is very difficult to get rid of traces of ether: it is inflammable, burning with a bright and highly luminous flame. (p. 127.) It extinguishes a taper, and is quite unrespirable. Water absorbs about one-eighth its volume of olefiant gas (100 C. I. of water take up 15.3, BERZELIUS), leaving an insoluble residue, which burns like light carburetted hydrogen. Alcohol and ether take up 2 volumes of this gas; oil of turpentine 2.5 volumes, and olive oil 1 volume, by agitation at common temperatures and pressures, but a residue is always left, having the characters of light carburetted hydrogen. (FARADAY.) Obtained, therefore, by the usual process, the gas appears to contain different proportions of light hydrocarbon and probably other vapors, differing at different periods of its evolution; and

according to Faraday, even the portion of gas absorbed by oil of turpentine, is not of one uniform composition. It is absorbed by sulphuric acid: in the course of several days, 1 volume of sulphuric acid absorbs between 80 and 90 of olefiant gas, and a peculiar compound results, capable of forming distinct salts. (Such compounds will be more particularly noticed under the articles *Naphthalin*, *Oil of Wine*, and *Sulphovinic Acid*.)

One volume of olefiant gas requires, for perfect combustion, three of oxygen. When sulphur is heated in one volume of this gas, charcoal separates, and two volumes of sulphuretted hydrogen result. As hydrogen suffers no change of volume by combining with sulphur, it follows that olefiant gas contains two volumes of hydrogen condensed into one; hence the quantity of oxygen required for its combustion. This gas is also decomposed by heat alone, as by passing and repassing it through a red-hot tube of earthenware or metal; it then gradually deposits its carbon, and is ultimately expanded into twice its original volume of pure hydrogen*. An analogous decomposition is observed of the olefiant gas generated in the retorts of gas-works, and is connected with the deposition of several interesting forms of carbon. (MARCHAND, *Chem. Gaz.*, June, 1843).

When *one* volume of olefiant gas is detonated by the electric spark in a proper tube (which, on account of the violence of the explosion, should be very strong), with three volumes of oxygen, *two* volumes of carbonic acid are formed, and water is deposited: now two volumes of carbonic acid contain two volumes of oxygen, so that the other volume of oxygen must have condensed two volumes of hydrogen to form water. Hence, *one* atom or volume of olefiant gas must contain *two* atoms of carbon, and *two* atoms or volumes hydrogen.

The following diagrams further illustrate the results of the combustion of one volume, or equivalent, of olefiant gas with three volumes (or six equivalents) of oxygen.



* When *oil-gas*, compressed into vessels by a power equal to that of 30 atmospheres, is suddenly allowed to escape through a small aperture into the air, the *expansion* which it suffers appears to occa-

sion in it a degree of chemical decomposition; for it deposits a black carbonaceous matter upon paper held in the current. (*Quarterly Journal*, N.S., i. 204.)

It is obvious, from the above statements, that olefiant gas must be composed of

					Saussure.		
Carbon	2	12	85.7	85
Hydrogen....	2	2	14.3	15
<hr/>			<hr/>				
Olefiant gas	1		14		100.0		100

Or, it may be thus represented:—

		Carbon.		
Hydrogen.	1	6	=	Olefiant Gas. 14
Hydrogen.	1	6		

OLEFIANT GAS AND CHLORINE. When olefiant gas is mixed with chlorine in the proportion of 1 to 2 by volume, the mixture, on inflammation, produces hydrochloric acid, and charcoal is abundantly deposited. If the gases be well mixed, and then inflamed in a tall and narrow glass jar (about 2 feet high and 4 inches in diameter), placed with its mouth upwards, the experiment is very striking; a deep-red flame gradually descends through the mixture, and a dense black cloud of carbon rises into the atmosphere; fumes of hydrochloric acid are at the same time formed, and a peculiar aromatic odor is evolved.

CHLORIDE OF OLEFIANT GAS. CHLORIDE OF ELAYLE. C_2H_2Cl . If instead of inflaming the mixture of one volume of olefiant gas and two volumes of chlorine, the gases be merely mixed, in equal volumes, over water, or in a clean and dry glass globe exhausted of air, they act slowly upon each other, and a peculiar fluid is formed, which appears like a heavy oil; hence the term *olefiant gas*, applied to this hydrocarbon by the Dutch chemists, and *Elayle* (from $\epsilon\lambda\alpha\iota\omicron\nu$ and $\upsilon\lambda\eta$, *the source of an oil*), by Berzelius. It also may be formed by allowing a current of each gas to meet in a proper receiver; but there should be excess of olefiant gas, for if the chlorine be in excess, the liquid absorbs it. To purify it, it should be washed in water, and then carefully distilled from fused chloride of calcium.

Chloric ether is the name applied to this fluid by Dr. Thomson, who, in 1810, ascertained that its component parts were chlorine and carburated hydrogen. It was afterwards examined by Robiquet and Colin (*Ann. Ch. et Ph.*, i. and ii.), and by Regnault (*Ann. Ch. et Ph.*, lxxix. and lxxx.) The term *Hydrochloride of Carbon*, or *Hydrocarburet of Chlorine*, has been applied to it; but as there are other combinations of the same elements, the term *Chloride of olefiant gas* is more explicit: it has also been called *Dutch liquid*. It is transparent and colorless; its taste sweet, and somewhat acrid; its odor fragrant; its specific gravity = 1.2. It boils at 152° . According to Gay Lussac the specific gravity of its vapor is 3.45. It burns with a green flame, evolving hydrochloric acid, and largely depositing charcoal. It is decomposed when passed through a

red-hot tube. As it is produced by equal *volumes* of chlorine and olefiant gas, it must be a compound of

						Volumes.	Sp.Gr.
Carbon.....	2	...	12	...	24	} Olefiant gas....	1 0.98
Hydrogen	2	...	2	...	4		
Chlorine	1	...	36	...	72		
<hr/>						Chlorine	1 2.47
Chloride of olefiant gas	1		50		100	1	3.45

Another view of the atomic constitution of this compound has been adopted by Regnault, which regards it as a combination of hydrochloric acid with the chloride of *acetyl*; the term *acetyl* being applied to a hypothetical hydrocarbon = C_4H_3 , which is considered as the base of acetic acid, to which, therefore, I must here refer: but in reference to the present question it will be obvious that 2 atoms of hydrochloride of carbon contain the elements of chloride of acetyl and hydrochloric acid, for $2[C_2H_2Cl] = C_4H_3Cl + HCl$. The origin and further application of these views will be apparent by reference to the theory of etherification, which is treated of under organic products: but they involve discrepancies in respect to the densities of olefiant gas and of the vapor of the hydrochloride, and confound olefiant gas with etherine or quadrihydrocarbon.

The action of chlorine on the olefiant chloride is attended by results which well illustrate the theory of substitutions (REGNAULT), and new compounds are found arising out of the abstraction of hydrogen and its replacement by chlorine. Of these compounds two are volatile liquids, containing $C_4H_3Cl_3$, and $C_4H_2Cl_4$, the action terminating in the production of sesquichloride of carbon ($471 = C_4Cl_6$ or $2[C_2Cl_3]$).

When the olefiant chloride is dissolved in an alcoholic solution of caustic potassa, and gently heated, chloride of potassium is deposited, and a peculiar gas or vapor escapes, which may be liquified at a temperature of 0° : it is C_4H_3Cl : it absorbs chlorine, producing $C_4H_3Cl_3$, and this again is resolved by the alcoholic solution of potassa into chloride of potassium, and a new volatile liquid = $C_4H_2Cl_2$.

OLEFIANT GAS AND IODINE. IODIDE OF OLEFIANT GAS. IODIDE OF ELAYLE. C_2H_2I . When iodine and olefiant gas are exposed to the action of light, they form a compound, first obtained by Faraday. (*Phil. Trans.*, 1821, p. 72.) Iodine and olefiant gas were put in various proportions, into retorts, and exposed to the sun's rays: after a while colorless crystals were formed, and a partial vacuum was produced: the gas in the vessels was found to contain no hydriodic acid. The compound was purified by introducing a solution of potassa into the retort, which dissolved the free iodine; the substance was then collected, washed, and dried.

The olefiant iodide is a white crystalline solid, fusible at 174° , and volatile without decomposition; its taste is sweet, and its odor aromatic. It is insoluble in water. It sinks in sulphuric acid of the specific gravity 1.84. It is a non-conductor of electricity. When highly heated it evolves iodine: it is not readily combustible, but when held in the flame of a spirit-lamp, burns, diminishing the flame, giving off abundance of iodine, and some fumes of hydriodic acid. It is soluble in alcohol and ether, and may be obtained in crystals from these solutions.

The alcoholic solution is of a sweet taste, but leaves a sharp sensation upon the tongue. Sulphuric acid does not dissolve it, but, when heated in the acid to between 300° and 400° , it is decomposed, apparently by the heat alone, and iodine and a gas (probably olefiant) are liberated. Boiling solution of potassa gradually decomposes it.

It was analyzed as follows, (*Quarterly Journal*, xiii.) Four grains were passed in vapor over heated copper in a green-glass tube; iodide of copper was formed, and pure olefiant gas evolved, amounting to 1.37 cubic inches, or 0.413 grains. Now 4 grains, *minus* 0.413 grains, leaves 3.587 of iodine, and $3.587 : 0.413 :: 126 : 14.3$ nearly; the constitution of this compound, therefore, is analogous to that of the hydrochloride of carbon; it may be regarded as composed of

Carbon	2	12	8.63	} Olefiant gas ...	1	14
Hydrogen	2	2	1.44				
Iodine	1	126	89.93		Iodine	1
<hr/>									
Iodide of olefiant gas ...	1		140		100.00		1		140

OLEFIANT GAS AND BROMINE. BROMIDE OF OLEFIANT GAS. BROMIDE OF ELAYLE. C_2H_2Br . When the preceding iodide of olefiant gas is added to bromine, a hissing noise is produced, with much heat, and a bromide of iodine and fluid compound of olefiant gas and bromine are formed. The bromide of iodine may be removed by water, and the olefiant bromide, with a slight excess of bromine, remains. It may be rendered colorless by a little alkali. If the iodide is in excess, subbromide of iodine is the principal result.

The pure olefiant bromide is a colorless liquid, heavier than water, of a penetrating ethereal odor, a sweet taste, and volatile. It does not change color by exposure to air. At 22° it becomes solid, and breaks like camphor. It was formed, by Balard, by letting a few drops of bromine fall into a flask of olefiant gas. (*Ann. Ch. et Ph.*, xxxiv.) It consists of

Carbon.....	2	12	13.04	} Olefiant gas	1	14
Hydrogen	2	2	2.18				
Bromine $\frac{1}{2}$	1	78	84.78		Bromine.....	1
<hr/>									
Bromide of olefiant gas	1		92		100.00		1		92

BICARBURET OF HYDROGEN. C_6H_3 . For our knowledge of this combination we are indebted to Faraday. (*Phil. Trans.*, 1825, p. 440.) When certain oils are passed through red-hot tubes, as in the process for making gas for the purpose of illumination, there is at the same time a vapor produced, which, by considerable pressure, and by cold, may be reduced to a liquid state. Large quantities of this liquid were obtained at the Portable Gas-works, by subjecting the gas produced by the decomposition of whale oil, to a pressure of 30 atmospheres; this occasioned the deposition of the fluid, which was drawn off by a valve: it effervesced as it issued forth, and by the difference of refractive power, a dense transparent vapor was seen at the same time descending through the air. This effervescence immediately ceased, and the liquid was readily retained in ordinary stoppered bottles. 1000 cubical feet of good gas yielded nearly one gallon of it. It appeared as a thin light fluid,

sometimes transparent and colorless, at others opalescent, being brown by transmitted, and green by reflected light; it had the odor of oil-gas. Its specific gravity was 0.821: it did not congeal when cooled down to 0° ; was insoluble in water, readily soluble in alcohol, ether, and oils; slowly decomposed by nitric acid; and formed peculiar combinations with sulphuric acid, afterwards to be noticed. This fluid Faraday found to be a mixture of various bodies, differing in their degrees of volatility; to separate them, he carefully distilled successive portions into receivers cooled to 0° , the receiver being changed with each rise of 10° in the retort, and the liquid retained in a state of incipient ebullition: it was thus found that the boiling-point was most constant between 176° and 190° , at which temperature considerable quantities passed over without any change in the degree. Of this rectified fluid a portion was exposed to a temperature of 0° , when part of it solidified, and being collected and dried by pressure, did not liquify till raised to 28° .

This portion constitutes the compound which we have above termed *Bicarburet of Hydrogen*. It appears as a colorless transparent liquid, having a peculiar odor like oil-gas mixed with that of bitter almonds. Its specific gravity is 0.85 at 60° . When cooled to a little below 32° , it solidifies, and contracts considerably on congealing. It does not conduct electricity; evaporates when exposed to air; boils at 186° *. The specific gravity of its vapor is 2.77, or compared with hydrogen as 39 to 1. 100 cubical inches, therefore, at mean temperature and pressure, would weigh about 85 grains. It is very slightly soluble in water, but readily soluble in alcohol and ether, and in oils. It burns with a bright flame and much smoke, and when put into oxygen furnishes sufficient vapor to form a detonating mixture. Passed through a red-hot tube, it is resolved into carbon and carburetted hydrogen gas. Placed in the sunshine in chlorine, heat is evolved, hydrochloric acid formed, and a solid and liquid are produced, which appear to be compounds of chlorine, carbon, and hydrogen. Iodine does not act upon it, but dissolves in it in small quantity, forming a crimson solution. Potassium exerts no action upon it at a temperature of 186° . Neither alkalis nor their carbonates act upon it. Nitric acid occasions in it little other change than the formation of a minute portion of hydrocyanic acid. Sulphuric acid added to it over mercury, exerted a moderate action; no heat was evolved, no blackening took place, no sulphurous acid was formed, but the acid became of a light-yellow color, and a portion of a clear colorless fluid floated, which appeared to be a product of the action, and which was not altered by water, and solidified at 34° , being then white and crystallized.

Faraday's attention was next directed to the *composition* of this substance: he decomposed it by passing its vapor over heated oxide of copper, by which it was resolved into carbonic acid and water; and a careful determination of their weights gave (as the mean of several experiments) 1 hydrogen and 11.576 carbon, as its components. Other

* The boiling-points of the hydrocarbons vary from 130° to 415° , and depend upon their composition: of two hydrocarbons containing the same number of atoms of carbon, that containing most hydrogen will have the lowest boiling-point; and

where the atoms of hydrogen are the same, but those of carbon vary, the boiling-point will be the highest where there is most carbon. (GERHARDT. *Ann. Ch. et Ph.*, Mai, 1845.)

experiments led to the conclusion, that in this substance the carbon and the hydrogen are in the mutual ratio of 12 to 1. But on examining the volume of oxygen requisite for the combustion of this substance, it was found that 100 volumes of its vapor required 750 of oxygen, and that the result was water, and 600 volumes of carbonic acid; so that to form the water 150 volumes of oxygen must have combined with 300 of hydrogen, and the remaining 600 volumes must have united with the carbon to form the 600 volumes of carbonic acid. Hence we must conclude, that although the ratio of the carbon to the hydrogen, in this compound, is as 12 to 1, it, in fact, consists of

	Atoms.			
Carbon	6	36 92·31
Hydrogen	3	3 7·69
<hr/>				
Bicarburet of hydrogen.....	1		39	100·00

Or, it may thus be represented—

Carbon.		Carbon.	
6	Hydrogen.	6	
Carbon.	1	Carbon.	
6	Hydrogen.	6	= Vapor of the Bicarburet. 39
Carbon.	1	Carbon.	
6	Hydrogen.	6	
	1		

A compound described by E. Davy, under the name of *bicarburet of hydrogen*, appears to be isomeric with the above: he obtained it from the black carbonaceous substance accompanying the potassium procured by intensely heating a mixture of carbon and carbonate of potassa: this substance appears to be a compound of potassium and carbon, and when acted upon by water, evolves a gas which burns with a brighter flame than olefiant gas, and explodes on mixture with chlorine: it is said to require 2·5 volumes of oxygen for its entire combustion, and to consist of 92·23 carbon and 7·67 hydrogen.

SESQUIHYDROCARBURET. In examining the liquid remaining after the separation at 0° of the preceding bicarburet, it was found to exhibit peculiarities which seem to identify it as a peculiar and definite compound; and from such experiments as were made upon it, it is probable that it contains carbon and hydrogen in the ratio of 3 to 2.

QUADRIHYDROCARBURET. ETHERINE. C₄H₄. It has already been stated, that a portion of the original oil-gas liquor is *volatile at common temperatures*; at the heat of the hand it passes off in vapor, and may be collected as a gas over mercury. It burns with a brilliant flame: its specific gravity to that of hydrogen is as 28 to 1; to that of common air as 1·963 to 1; and 100 cubic inches weigh 59·3 grains. It condenses into a liquid when cooled to 0°, and enclosed in this state in a tube of known capacity, and hermetically sealed, the bulk of a given weight of it

at common temperatures was ascertained: this, compared with water, gave its specific gravity as 0.627 at 54°; so that among solids or liquids it is the lightest body known. It scarcely dissolves in water, but readily in alcohol, and the solution effervesces from the escape of vapor when water is added. It is abundantly condensed by sulphuric acid. One volume of the acid condenses above 100 volumes of the vapor, producing great heat, but no sulphurous acid. The solution is dark-colored, has a peculiar odor, and evolves no gas upon dilution. By detonation with

Carbon.		=	Etherine.
Hydrogen.	6		
1	Carbon.		
Hydrogen.	6		
1	Carbon.		28
Hydrogen.	6		
1	Carbon.		
Hydrogen.	6		
1			

oxygen, it was found that 1 volume of the vapor required 6 volumes of oxygen for perfect combustion, giving rise to 4 volumes of carbonic acid. The remaining 2 volumes of oxygen must have combined with 4 of hydrogen to form water. Upon which view, 4 volumes or equivalents of hydrogen = 4, are combined with 4 equivalents of carbon (6×4) = 24, to form 1 volume of the vapor, the specific gravity of which, compared with hydrogen, would be 28, which is also its equivalent or atomic weight; so that the volume of etherine and its components may be represented as in the margin,

and it consists of

Atoms.					
Carbon	4	24 85.71
Hydrogen	4	4 14.29
<hr/>					
Etherine	1		28	100.00

CHLORIDE OF ETHERINE. As the relative proportions of the elements in this compound are the same as in olefiant gas, it became interesting to ascertain whether chlorine had the same action upon it. Chlorine and the vapor were therefore mixed in an exhausted retort, heat was evolved, and a liquid resembling chloride of olefiant gas formed; but it could not be identified with it, inasmuch as it consisted of nearly equal volumes of the vapor and of chlorine; and, therefore, contained twice as much carbon and hydrogen. When treated with excess of chlorine in sunlight, hydrochloric acid was formed, and chlorine absorbed; a peculiar fluid was also produced, consisting of hydrogen, chlorine, and carbon, but no chloride of carbon. It seems not improbable that a compound of etherine and chlorine corresponding with that of olefiant gas and chlorine may exist, and this would agree with Regnault's formula, $C_4H_4Cl_2$. The elements of this chloride of etherine would be perfectly consistent with those of a combination of hydrochloric acid with chloride of acetyl; in which case etherine might be represented as a hydruret of acetyl, or as C_4H_3H , which, when exposed to chlorine, absorbs 2 volumes or equivalents; so that a chloride of acetyl and hydrochloric acid are formed, giving rise to $C_4H_3Cl + HCl$. In other words, etherine, losing an atom of hydrogen, becomes acetyl, and if that atom of hydrogen be replaced by

an atom of chlorine, chloride of acetyl is formed; if the displaced atom of hydrogen also combine with an atom of chlorine, it produces an atom of hydrochloric acid, which, combined with the chloride of acetyl, produces the hydrochlorate of chloride of acetyl, the elements of which are those of a bichloride of etherine. Regnault further finds, that when the hydrochlorate of chloride of acetyl is subjected to the further action of a stream of chlorine, another atom of hydrogen is carried off as hydrochloric acid, and an atom of chlorine left in its place; thus $C_4H_3Cl + HCl$, becomes $C_4H_2Cl_2 + HCl$, and by the continuous action of chlorine the whole of the hydrogen is ultimately carried off as hydrochloric acid, and sesquiperchloride of carbon $= C_4Cl_6$, or $2 [C_2Cl_3]$ remains.

Faraday's researches, in reference to these forms of hydrocarbon, established the important fact that substances may exactly resemble each other in the relative proportions of their constituents, and yet, in consequence of peculiarities in their atomic arrangement, exhibit distinct physical and chemical properties, presenting, as already remarked, instances of isomerism. Thus, in etherine and in olefiant gas, the carbon and hydrogen are in the ratio of 6 to 1; but, in the former, the elements are united in the proportion of 24 to 4, and in the latter of 12 to 2. It has been observed by Dr. Turner, that this peculiarity is explicable on the supposition that the ultimate elements of such compounds are differently disposed. "It is to be presumed that the smallest possible particle of olefiant gas contains 2 atoms of carbon, and 2 of hydrogen; and that, in like manner, an integrant particle of etherine contains 4 atoms of each element. Neither of these substances could, I conceive, be formed by the direct union of a single atom of carbon and a single atom of hydrogen. If a combination of the kind were to occur, a new compound, different from any known at present, would be the result."

In respect to the nomenclature applicable in these cases, there is obviously much difficulty. The compound of 2 atoms of carbon and 2 of hydrogen might be called *bihydrocarbon*; the designation *olefiant gas* is still generally retained, but the term *Elayle*, having the same meaning, and being shorter, is perhaps preferable, especially as it is applicable to the compound considered as a radical. For the compound of 4 atoms and 4, the term *quadrocarburetted hydrogen* has been proposed, but that would rather imply it to consist of 4 atoms of carbon and 1 of hydrogen, than of 4 and 4; the term *quadrihydrocarbon* or *quadrihydrocarburet*, has, therefore, been substituted; but perhaps *etherine* is less objectionable, implying its hypothetical relation to *ether*.

TERHYDROCARBON. SUPEROLEFIANT GAS. C_3H_3 . It seems probable that a hydrocarbon, the vapor of which contains in 1 volume 3 atoms of hydrogen and 3 of carbon, is occasionally produced during the destructive distillation of oil; and Henry (*Phil. Trans.*, 1821, p. 156) adverts to such a compound, discovered in oil-gas by Dalton. Thomson describes it under the name of *tritocarbohydrogen*; but till some definite mode of obtaining it has been pointed out, and its properties experimentally ascertained, its distinct existence must remain doubtful.

NAPHTHA. C_6H_5 . The products usually designated by the term *Naphtha* are mixtures of various hydrocarbons, some of which may be

separately obtained by carefully graduated ebullition. The term *naphtha* might be limited to a liquid hydrocarbon, yielding a vapor of the density of 2·8, and containing carbon and hydrogen in the atomic relation of 6 to 5. Such a hydrocarbon is both a natural and artificial product. Natural naphtha is obtained in considerable quantity at Baku, near Derbent, on the north-west shore of the Caspian Sea. The soil is a clayey marl, and so impregnated with naphtha, that, when turned up to the depth of a few inches, it will inflame on the application of a lighted candle; in this soil pits are sunk, in which the naphtha collects in considerable quantities. The purest European naphtha comes from Monte Ciaro, near Piacenza, in Italy: this hill consists of horizontal beds of argillite, in which pits are sunk till the water comes in, upon the surface of which the naphtha oozes and collects, and is occasionally skimmed off. An inferior kind is produced at Monte Festino, near Modena. A similar liquid may be obtained by the distillation of *petroleum*, or mineral tar, a substance which will be described among Bitumens.

Coal-oil, or *coal-naphtha*, is a product somewhat resembling the former; it is one of the results of the destructive distillation of pit-coal, some of the varieties of which yield it in large quantities; it is extremely volatile, and therefore generally passes on with the gas to the remoter parts of the condensing-apparatus, and often collects in the gas-meters and gasometer-tanks, and even in the first branches of the mains, from the syphons of which it is sometimes drawn off. When purified by distillation it is a colorless limpid liquid.

The properties of naphtha differ according to the sources whence it is obtained, but when carefully rectified at a given temperature, and purified by distillation with water, it appears to possess the same leading characters and composition: indeed, it is probable that natural and artificial naphtha are of one origin, the former being derived from volcanic, the latter from ordinary distillation. The specific gravity, however, of the purest Persian and Italian naphtha is said to vary from ·750 to ·760, while that of coal naphtha rises to ·820, or higher. The odor of the former is bituminous, but not disagreeable; that of the latter, penetrating and unpleasant. It does not congeal at 0°. Upon the approximation of a flaming body, naphtha takes fire and burns with a voluminous, and very sooty, and difficultly-extinguishable flame. It communicates odor to, but is not soluble in, water; it dissolves in absolute alcohol, and in ether, petroleum, and oils. When pure, it is not acted on by potassium or sodium, and is, therefore, used to preserve those metals from oxidation. The boiling-point of naphtha varies. Dr. Thomson states the boiling-point of Persian naphtha to be 320° to 352°; Dumas places it at about 365°. The density of its vapor is about 2·8. It dissolves the greater number of the essential oils, and the resins, and a little phosphorus and sulphur, and corrodes cork; it is remarkable for its property of dissolving caoutchouc, which first swells up, and then gradually gelatinizes, when digested in it with the aid of a gentle heat: in this pulpy state it is used to render various articles of clothing *water-proof*; the goods are stretched out, and varnished over with it, and then their varnished sides are applied to each other, and made to adhere by powerful pressure, so as to form a compound fabric or texture: the manufacture is completed, and the solvent driven off, by exposure to a moderate heat. This important and

well-known application of the solution of caoutchouc in naphtha, or coal-oil, was first suggested by Mr. Macintosh, of Glasgow. Among other sources of naphtha, or at least of a liquid hydrocarbon closely resembling it in all its leading properties, we may enumerate caoutchouc itself, which yields it by destructive distillation. (See *Caoutchouc*.) The ultimate composition of naphtha has been variously stated, probably from the difficulty of obtaining it in one definite state, but all analysts agree in representing it as a true hydrocarbon. According to Dumas, a definite compound, having all the characteristic properties of naphtha, is obtained by depriving *spirit of turpentine* of its oxygen, by the action of potassium, and then subjecting it to careful distillation. (*Ann. Ch. et Ph.*, L. 238.) When the vapor of these hydrocarbons has the density of 2·87, 1 volume of it may be regarded as containing 6 atoms of carbon, and 5 atoms or volumes of hydrogen.

Hence naphtha, or a hydrocarbon so constituted, would consist of

	Atoms.				
Carbon	6	36	87·80
Hydrogen.....	5	5	12·20
	<hr/>		<hr/>		<hr/>
	1		41		100·00

Or, by volume,

Carbon.		Carbon.		=	<div style="border: 1px solid black; padding: 5px; display: inline-block;"> Naphtha Vapor. 41 </div>
6	Hydrogen.	6			
	1				
	Hydrogen.				
Carbon.	1	Carbon.			
6	Hydrogen.	6			
	1				
	Hydrogen.				
Carbon.	1	Carbon.			
6	Hydrogen.	6			
	1				

NAPHTHALIN. $C_{10}H_8$. This name was first given by Dr. Kidd (*Phil. Trans.*, 1821, p. 209,) to a concrete crystalline substance found among the products of the coal-gas manufacture; it may be obtained by subjecting coal-tar to distillation; it passes over after the naphtha or coal-oil: when any of the varieties of the tar are so distilled that their vapor may be exposed to a high temperature, more or less naphthalin is formed. I first pointed it out as a binary compound of carbon and hydrogen, in 1819. (*Quar. Journ.*, viii. 287.) It was afterwards examined by Chamberlain. (*Ann. of Philos.*, xix.) It is generally first obtained in translucent flakes of a red or brown color. By slow sublimation with a portion of powdered charcoal, it may be obtained colorless, and nearly inodorous;

but when heated, it exhales a peculiar faint odor, which has been compared to that of the flower of the narcissus. Its taste is slightly aromatic; its specific gravity is about 1.05; it is unctuous to the touch, and slowly evaporates at common temperatures. It fuses at about 176° , and crystallizes as it cools; at about 420° it boils and distils over, with little change: but is also carried over in vapor when distilled with water. When inflamed, it throws off a singularly large quantity of black smoke, which diffuses itself in light films of carbon through the air. It is insoluble in cold, and very slightly soluble in boiling water; alcohol, ether, the oils, and naphtha, dissolve it abundantly, and from its hot alcoholic solution it is deposited in iridescent crystals. The alkalis have no action on naphthalin: when long boiled in nitric acid, it is slowly altered, and a part of the acid decomposed: hot hydrochloric acid dissolves it very sparingly; acetic and oxalic acids more copiously: sulphuric acid dissolves and combines with it.

The proportions of carbon and hydrogen which constitute naphthalin were first determined by Faraday, and his results subsequently confirmed by Liebig, Wöhler, and Laurent. The specific gravity of its vapor is 4.49, or compared with hydrogen, as 64 to 1, so that 100 cubic inches should weigh 135 grains. Its components are

	Atoms.				
Carbon	10	60	93.75
Hydrogen....	4	4	6.25
<hr/>			<hr/>		
Napthalin....	1		64		100.00

Or,	Carbon.		Carbon.	=	<div style="border: 1px solid black; padding: 5px; display: inline-block;"> Naphthalin Vapor. 64 </div>
	6	Hydrogen.	6		
	Carbon.	1	Carbon.		
	6	Hydrogen.	6		
	Carbon.	1	Carbon.		
	6	Hydrogen.	6		
	Carbon.	1	Carbon.		
	6	Hydrogen.	6		
	Carbon.	1	Carbon.		
	6		6		

NAPHTHALIN AND CHLORINE. The mutual action of chlorine and naphthalin has been examined by Laurent. (*Ann. Ch. et Ph.*, lii. 275.) When naphthalin is subjected to the action of chlorine it fuses and forms two chlorides. The protochloride = $C_{10}H_4Cl$, is an oily liquid; the bichloride = $C_{10}H_4Cl_2$, is a crystalline solid; it may be purified by boiling ether, which deposits it on cooling in transparent rhomboids. It fuses at 320° , and in close vessels boils and is decomposed; but when carefully heated in a current of air, it may be volatilized without decomposition.

The *liquid chloride*, obtained by the evaporation of its ethereal solu-

tion, is yellow; insoluble in, and heavier than water: it is soluble in alcohol and ether, and may be distilled without decomposition.

In describing these compounds, naphthalin is conveniently represented as $\text{C}_{20}\text{H}_{18}$, and by the successive substitution of chlorine for hydrogen in such a compound, a great variety of products are obtained, which Laurent has named and examined: the details of these elaborate researches scarcely admit of intelligible, and much less of useful, abridgement, but they are curious as illustrations of the doctrine of types and substitutions, and of nomenclatural ingenuity: a condensed account of them is given by Dr. Gregory (*Outlines of Chemistry*), to which, and to the original essays of Laurent and Dumas, I must refer the reader. So also in reference to the parallel compounds of naphthalin and bromine.

NAPHTHALIN AND NITRIC ACID. The action of nitric acid on naphthalin has also been studied by Laurent. (*Ann. Ch. et Ph.*, lix. 381.) It gives rise to a series of compounds, in which NO_4 is substituted for hydrogen, and of which an abridged account will also be found in Gregory's *Outlines*.

NAPHTHALIN AND SULPHURIC ACID. SULPHONAPHTHALIN. SULPHONAPHTHALIC ACID. $\text{C}_{20}\text{H}_{18} + 2\text{SO}_3$. The action of sulphuric acid on naphthalin was first investigated by Faraday. (*Phil. Trans.*, 1826.) Naphthalin was fused with half its weight of sulphuric acid, which, on cooling, formed a red crystalline compound, soluble in water; carbonate of baryta was added to its solution, by which sulphate and sulphonaphthalate of baryta were formed; the former insoluble, but the latter soluble; its solution was filtered off, and sulphuric acid added to it sufficient to precipitate the baryta. An aqueous solution of sulphonaphthalic acid was thus obtained, of a bitter acid taste, and powerfully reddening litmus: concentrated by evaporation it became brown, thick, and, ultimately, solid and very deliquescent. By renewed heat it melted and charred, but did not flame, and ultimately gave sulphuric and sulphurous acid vapors, and left charcoal. Another portion of the acid was evaporated under an exhausted receiver, including a vessel of sulphuric acid. In some hours it became a white soft solid, apparently dry, and after a longer period was hard and brittle. In this state it was deliquescent in the air, but might be preserved unaltered in a close vessel. Its taste was bitter, acid, and metallic: when heated to 212° it melted, and crystallized and solidified as it cooled: more highly heated, water passed off, and it assumed a red tint; further heated, it became brown and black, and naphthalin, sulphurous acid, and charcoal were evolved. This acid dissolves in water, alcohol, and oils. Its aqueous solution forms neutral salts with bases, all of which are soluble in water, most of them in alcohol, and all combustible, leaving sulphates or sulphurets, according to circumstances.

To determine the composition of this acid, its neutral salt with baryta was chiefly experimented upon: and the following appeared to be its elements:

Baryta	1	...	77	...	27.0
Sulphuric acid	2	...	80	...	28.1
Carbon	20	...	120	...	42.1
Hydrogen	8	...	8	...	2.8
<hr/>					
Sulphonaphthalate of baryta	1		285		100.0

So that the composition of sulphonaphthalic acid would be

Carbon	20	120	57·8
Hydrogen	8	8	3·8
Sulphuric acid.....	2	80	38·4
<hr/>					
Sulphonaphthalic acid.....	1		208		100·0

Of the two proportionals, therefore, of sulphuric acid, one is, as it were, saturated by the hydrocarbon, for it only combines with 77 of baryta, which is the equivalent of one atom of that base. This property of hydrocarbon, indicating its capability of uniting to an acid, saturating it, and performing, as it were, the part of a base, has been more extensively inquired into and illustrated by Hennell; his experiments relate chiefly to certain combinations concerned and developed in the formation of *ether*, under which article the details will be given.

Faraday's sulphonaphthalic acid has been subsequently represented as containing the hyposulphuric instead of sulphuric acid, and as represented therefore by $C_{20}H_8S_2O_5,HO$. It is stated that when his acid is saturated by carbonate of lead, an insoluble sulphate is formed, together with two soluble salts, one of which is soluble in alcohol, and is $C_{20}H_8S_2O_5,PbO$, and the other insoluble in alcohol = $C_{11}H_4S_2O_5,PbO$: it is further assumed that a third acid accompanies these.

Anhydrous sulphuric acid, passed in vapor over fused naphthalin, forms a red liquid, *hydrosulphoglutinic acid*, which, when pure and dry, is a hard glassy mass; and if there be excess of naphthalin, two neutral bodies are at the same time formed, *sulphonaphthaline*, which is a crystalline fusible solid, and *sulphonaphthalide*, a crystalline powder not fusible at 212° .

PARANAPHTHALIN. Under this term Dumas and Laurent (*Ann. Ch. et Ph.* L. 187) have described a hydrocarbon closely resembling naphthalin in all its essential properties, but yielding a vapor having the density of 6·78. Paranaphthalin is less volatile than naphthalin, and, therefore, when coal-tar is distilled, it is among the latter of its products. According to Reichenbach (*Poggend. Ann.*, xxviii. 484), paranaphthalin is a mixture of naphthalin and another definite hydrocarbon, which he terms *paraffine*, and will be described amongst organic products. The term *anthracene* has subsequently been applied to paranaphthalin, and it has been represented as $C_{30}H_{12}$.

Among the last portions of the distillation of coal-tar, a yellow crystalline solid is found, fusing at 455° , and insoluble in most liquids; it has been termed *chrysene*, and its formula is said to be $C_{12}H_4$: it is accompanied by a more fusible substance, *pyrene* = $C_{15}H_3$.

When bituminous shale is distilled, it yields several oily products, among which one has been called *ampeline*: it dissolves in alcohol, but a few drops of water cause it to separate.

IDRIALIN. This term is applied by Dumas to a native hydrocarbon, found in the mercury-mine of Idria, in Carniola, and which appears to be very analogous to naphthalin: it is said to consist of 3 atoms of carbon and 1 of hydrogen. (*Ann. Ch. et Ph.*, L. 193.)

GAS ILLUMINATION: COAL-GAS. Mixtures of some of the hydrocarbons now described, and other gaseous compounds, are abundantly produced during the destructive distillation of coal; and the gases thus obtained are employed for the purposes of illumination, as economical substitutes for oil, tallow, &c. This distillation of pit-coal is a process carried on upon a very extensive scale. The coal is placed in oblong cast-iron cylinders, or *retorts*, which are ranged in furnaces, to keep them at a bright-red heat, and the volatile products are conveyed by a common tube, usually termed the *hydraulic main*, into a *condensing vessel*, kept cold by immersion in water; and in which the water, tar, ammoniacal liquor, and other condensible vapors, are retained: the gaseous products consist principally of varieties of carburetted hydrogen, with more or less sulphuretted hydrogen, and carbonic oxide, carbonic acid, hydrogen, nitrogen, and cyanogen: these are passed through or over hydrate of lime, or through a mixture of quicklime and water*, in vessels called *purifiers*, by which the sulphuretted hydrogen and carbonic acid gases are absorbed, and the carburetted hydrogen gases transmitted sufficiently pure for use into *gasometers*, whence the pipes issue for the supply of streets, houses, &c. The coke remaining in the retorts is a valuable fuel†.

It would be out of place here to describe in detail the *plant* or arrangements of an extensive gas manufactory, and indeed some of the larger establishments in and about London should be visited, in order to acquire a just notion of the machinery and its management: much useful information upon this subject will be found in Dr. Ure's *Dictionary* and its *Supplement*; and in Dumas' *Chimie appliquée aux Arts*.

* Mr. Parker, of Liverpool (*Phil. Mag.* vol. iii. p. 292,) proposed to pass the gas, as it comes from the coal retorts, through red-hot iron tubes, by which the contaminating gases and vapors are further decomposed, and the quantity of useful gas increased. This suggestion, if it succeeded, would greatly diminish the quantity of tar; but as carburetted hydrogen is decomposed at a red heat, it would, probably, tend to diminish the illuminating power of the gas. The *purification* of coal-gas is a subject of the utmost importance, especially as relates to perfectly freeing it from sulphuretted hydrogen, which if present produces *sulphurous acid* during combustion, and is, therefore, highly noxious; in the case of the escape of unburnt gas, sulphuretted hydrogen is an equal evil; it is fetid and unwholesome, and it causes the immediate tarnishing of silver and other metals: its presence is fortunately easily detected by a piece of paper moistened with a solution of sugar of lead, and no gas should be allowed to be burned, which *blackens* that test. Coal-gas, however, though free from sulphuretted hydrogen, occasionally produces a little sulphurous acid when burned, and in such cases I suspect the presence of the vapor of sulphuret of carbon. Ammonia or some ammoniacal compound is also often found in coal-gas

even after it has been deprived of all sulphur; its presence is very injurious to copper tubes and brass stop-cocks. It has been proposed to free the gas from this contamination by passing it through dilute sulphuric acid, or through a solution of alum, and lately this plan has been extensively adopted, and the resulting sulphate of ammonia has been used as a source of sal ammoniac and other products, and has been extensively employed as a manure.

† On the 1st January, 1837, there were in London and the suburbs 30 gas-works employing a capital of 2,800,000*l.*, and deriving a yearly rental of about 450,000*l.*, using annually about 180,000 tons of coal, and producing about 1460 million cubic feet of gas. There were in these works about 176 gas-holders, the united contents of which exceeded 5,500,000 cubic feet; they supplied about 165,000 lamps. According to Ure (*Dictionary*) the consumption of gas nearly doubled itself between 1822 and 1827, and again between 1827 and 1837. He further states that in London 800 tons of coal are used in the retorts on the shortest day in 24 hours, and that 7,120,000 cubic feet of gas are consumed in the longest night, say the 24th of December. About 2500 persons are employed in the metropolis alone in this branch of manufacture.

The specific gravity of purified coal-gas is liable to much variation: sometimes it falls below 0·450, and at others exceeds 0·650. These differences are partly referable to the nature of the coal, but chiefly to the manner in which the process of distillation is conducted, as to duration, and temperature: it has already been remarked, that when the varieties of hydrocarbon are passed through highly-heated tubes, they are more or less perfectly decomposed into carbon and hydrogen; hence the gas which is obtained at a high temperature, or which, after its formation, has been in contact with red-hot surfaces, is apt to be partly decomposed; it is thus increased in bulk, but diminished in specific gravity, and in illuminating power; hence, too, analysis detects in coal-gas, more or less uncombined hydrogen. The best kind of coal for distillation is that which contains most bitumen and least sulphur. The chaldron should yield about 12000 cubical feet of purified gas, of which each Argand's burner, equal to six wax candles, may be considered as consuming from four to five cubical feet per hour.

OIL-GAS. Some years ago, Messrs. J. and P. Taylor invented an apparatus for the conversion of oil into gas. It consists of a furnace with a contorted iron tube containing fragments of brick or coke, passing through it, into which, when red-hot, the oil is suffered to drop; it is decomposed, and converted almost entirely into charcoal, which is deposited in the tube, and into a mixture of carburetted hydrogen gases and vapors, of which from two to three cubic feet may be regarded as equivalent to five or six of coal-gas, for the production of light. (*Quarterly Journal*, vol. viii.) The commonest whale-oil, or even pilchard-dregs, quite unfit for burning in the usual way, afford abundance of excellent gas, requiring no other purification than passing through a refrigerator, to free it of its more condensible vapors. A gallon of whale oil affords about 90 cubical feet of gas of an average specific gravity of 0·900, and an Argand burner, equal to seven candles, consumes a cubical foot and a half per hour. If its specific gravity exceed 0·900, it may be considered as containing too large a proportion of the heavier hydrocarbons, by which the bulk of the produce is much diminished, which are apt to condense in the pipes and gasometer, and which also occasion a fuliginous deposit during the consumption of the gas in ordinary burners. Oil as well as resin-gas, frequently contains carbonic acid to the amount of 8 or 10 per cent., which deteriorates its illuminating power.

RESIN-GAS. In consequence of the high and generally fluctuating price of oil, it became an important object to obtain a gas, of equal brilliancy and purity to that which it affords, from materials at once cheaper and less liable to fluctuations of value; and with this view, attempts were made to decompose resin, in the apparatus above described. For this purpose melted resin was substituted for the oil; but the exit-pipes, by which the gas flowed off, soon became choked with a thick bituminous substance, which stopped the process; and the product of gas was small, and of inferior quality. Mr. Daniell overcame this difficulty, by the invention of an apparatus, for which he obtained a patent. The exit-pipe of the oil-gas apparatus rose from the upper part of the retort, and was purposely carried to a considerable height, that the volatile oil, which was condensed during the process, might flow back and add to the product

of gas by its decomposition. It was the return of the volatile oil from resin, which choked up the pipes, when that substance was employed; and Mr. Daniell, observing this, led the exit-pipe from the *under* part of the retort into the hydraulic main, so that the return of any condensed vapor was rendered impossible. His mode of treating the resin is to dissolve, with the assistance of a gentle heat, about 8 lbs. in a gallon of the essential oil, which is plentifully formed during the decomposition of oil for making gas, or of resin itself. This solution is allowed to trickle into the heated retort half-filled with coke. A small diaphragm, just behind the exit-pipe, and filling half the diameter of the retort, prevents any of the liquid flowing into the hydraulic main. When the process is properly conducted, about 1000 to 1200 cubic feet of gas are obtained from the cwt. of resin, and rather more than the original quantity of volatile oil is condensed, which is again employed for the solution. It is necessary to add a small quantity of lime to the essential oil, to neutralize a little acetic acid, which is formed during the process. The apparatus works perfectly free from all obstruction. The gas thus formed is equal in quality to oil-gas of 100 cubic feet to the gallon. Its average specific gravity is 0.850; it requires no purification; and its smell is rather resinous, and not nearly so offensive as that of either oil or coal gas. Two cubic feet are equal in illuminating power to above five of the common coal-gas, and the expense of the material from which it is made, is not above one-third of the expense of oil. The sources of supply are as inexhaustible, and more generally distributed, than those of coal; and the forests of America, France, Spain, and Italy, yield the turpentine in quantities only limited by the demand. Many large towns in this country, in America, France, Holland, and the Netherlands, at one time adopted the use of this gas, but the late improvements in the production of coal-gas have led to the abandonment both of it and of oil-gas. The elegance and simplicity, however, of the manufacture, and the comparatively small capital required for the erection of the works, may, in some situations, give it a preference.

COMPOSITION AND ANALYSIS OF THE GASES USED FOR ILLUMINATION. ECONOMY OF GAS ILLUMINATION, &c. Dr. Henry's researches are the most important in reference to the philosophy of the art of gas-illumination, (NICHOLSON'S *Journal*, 1805; *Phil. Trans.*, 1808 and 1821, and 1824,) and much interesting matter connected with the subject will be found in an essay by Dr. Turner and Dr. Christison. (*Edin. Phil. Jour.*, 1825.) The treatises of Accum, and of Peckston, and Dr. Ure's *Dictionary*, contain an account of the apparatus, with details as to its construction and expense, together with much useful practical information. (See also DUMAS, *Chim. app. aux Arts.*)

The analysis of a mixture of hydrogen with carbonic oxide, carbonic acid, and hydrocarbon, often requires to be performed in investigations relating to the gases used for illumination; it may be approximately effected as follows: A hundred measures of the gas are introduced into a graduated tube, and the carbonic acid absorbed by a solution of potassa; the remaining gas is then transferred to thrice its volume of chlorine of known purity, standing over water in a tube of about half an inch diameter, and excluded from the solar rays; after 24 hours the hydro-

carbons and the excess of chlorine will have been absorbed, especially after a little agitation, and the remaining gas, if it consist of carbonic oxide and hydrogen only, may be analyzed by detonation with oxygen in excess; the measure of carbonic acid formed being equal to that of the original carbonic oxide. This proceeding depends upon the non-formation of chlorocarbonic acid in a mixture of carbonic oxide and chlorine in the contact of water, and out of the direct agency of the solar rays. Such mixture may be kept several days, occasionally renewing the chlorine as it becomes absorbed by the water, without any diminution in the bulk of the carbonic oxide. In these cases it is necessary to ascertain the purity of the chlorine by its absorption by water, and to take care that no hydrocarbon has escaped its action.

But in consequence of the presence of other compounds of carbon and hydrogen in coal, and especially in oil and resin gases, the accurate analysis of these complicated products becomes a problem of some difficulty. Dr. Henry's papers (in the *Phil. Trans.*, for the years 1818, 1820, and 1824, and in the *Annals of Phil.*, vol. xv.) contain details upon the subject, which the student should carefully consult. The removal of the hydrocarburetted vapors from these gases may, as Faraday has shown (*Phil. Trans.*, 1825, page 461), be effected by the agency of sulphuric acid: this also absorbs olefiant gas, but much less rapidly than the vaporous compounds; and if the gas under examination be diluted with three or four times its bulk of common air or of hydrogen, and excluded from the sunshine, the absorption of olefiant gas by the acid will be prevented. The hydrocarburetted vapors may also be removed by subjecting the gas to the action of olive-oil already saturated with olefiant gas.

As far as concerns the comparative value of different hydrocarburetted gases for the purpose of illumination, it seems evident, from Dr. Henry's experiments, that, whatever be their source or composition, it may be most accurately determined by the quantity of oxygen required to saturate equal volumes. In other words, the illuminating powers of the different gases will be proportional to the number of volumes of carbon condensed into one volume of the gas; and of these the oxygen consumed, and the carbonic acid produced, afford an accurate measure. (HENRY'S *Elements*, 1826, vol. i. 432.) "If 100 volumes, for instance, of one gas, require for perfect combustion 100 volumes of oxygen, and 100 volumes of another gas take 200 of oxygen, the value of the second will be double that of the first. Specific gravity, though a guide to a certain extent, is not a sufficient one; for the weight of a gas may be owing to a large proportion of carbonic oxide, which only gives out a very small quantity of light. Photometrical experiments also appear to require greater perfection in the instruments that have been invented for that purpose, before we can implicitly trust to results obtained by their means: but there can be no fallacy in the combustion of these gases by oxygen, if conducted with ordinary care, and especially if in each instance an average be taken of two or three trials, which need not occupy more than a few minutes. Nor can it admit of doubt, that, other circumstances being equal, the brilliancy of light evolved by the combustion of gases which are constituted of purely inflammable matter, will bear a proportion to their densities, perhaps even a greater proportion than one strictly arithmetical; because, while, by the combustion of denser gases, a higher temperature is

produced, the cooling agencies remain the same. It is probable, therefore, that of two gases composed of the same ingredients, that which has a double density will afford somewhat more than a double quantity of light.”

The illuminating value of coal-gas may be increased by saturating it with the vapor of coal naphtha, which is effected by passing it through a box containing sponge imbued with naphtha, or otherwise so constructed as to expose a large surface of naphtha to the passing gas. Mr. Lowe, who has patented this process, has applied it in several club-houses and other establishments requiring large quantities of gas. The illuminating power of naphthalized-gas compared with that of coal-gas, will depend upon the temperature of the gas as influencing the quantity of naphtha vapor which it holds. Thus at 75°, the naphtha vapor is in excess, and the gas burns with smoke when any common burner is used ; at 65°, the illuminating power is about doubled; at 55° or ordinary mean temperature, it is as 3 to 2; at 45° as 2·5 to 2; at 35° there is no perceptible difference. When the illuminating power is as 3 to 2, at 55°, the heating power of the naphthalized-gas is to that of coal-gas for equal quantities of light, as 3 to 4. Care must be taken in using naphthalized gas to employ proper burners, and the naphthalizing box should be placed in a cellar or other situation where the temperature is at least as low as that of the pipes through which the gas has afterwards to pass, otherwise the vapor may condense in their ramifications, and prove inconvenient.

The economy of gas-illumination may be judged of by examining the value of the products of distillation of a chaldron of coals, the average cost of which may be considered as 25s. It should afford—

	£	s.	d.
1¼ chaldron of coke, at 13s.....	0	16	3
24 gallons of tar, ammoniacal liquor, and other products, at 1d.	0	2	0
12000 cubic feet of gas, at 10s. per 1000 C.F.	6	0	0
	£6	18	3

These products are perhaps taken at their highest value, but they afford ample grounds for showing the advantage of gas-illumination, not merely for public purposes, but also in extensive private establishments. It appears that where more than one hundred lights are required, a coal-gas apparatus will be found profitable.

The cost of a lamp, fed by gas, and giving the light of seven	s.	d.
candles, will be	0	0¾ per hour.
Of Argand’s lamp, with spermaceti oil	0	3
Mould-candles.....	0	3½
Wax-candles	1	2

The following Table by Dr. Ure shows the relative intensities of light afforded by the combustion of different tallow candles, as compared with an Argand oil flame :—

Number in a Pound.	Duration of a Candle.	Weight in Grains.	Consump- tion per Hour: Grains.	Proportion of Light.	Economy of Light.	Candles equal to 1 Argand.
10 mould	5h. 9m.	682	132	12¼	68	5·7
10 dip	4 36	672	150	13	65½	5·25
8 mould	6 31	856	132	10½	59½	6·6
6 ditto	7 2½	1160	163	14⅔	66	5·
4 ditto	9 36	1787	186	20¼	80	3·5
Argand oil-flame	512	69·4	100	

According to Dr. Ure, a pint of the best sperm oil, weighing about 13 ounces, burns, in a well-trimmed Argand, about 10 hours*. But in some experiments made by Mr. J. T. Cooper, Mr. R. Phillips, and myself, we found the average consumption of the best sperm-oil by a well-trimmed Argand burner of the ordinary dimensions (about 1 inch diameter) to amount to about 800 grains per hour; it gave light equal to that of between ten and eleven spermaceti candles of six to the pound, each consuming about 140 grains of spermaceti per hour. We found that the

* The following answers to some questions put by the Committee of the Athenæum Club to Mr. Faraday, are so generally applicable, that I venture to introduce them here. “ Q. What is the ratio of light of an oil and gas burner?—In an excellent Argand oil lamp, compared with a 15-hole gas burner, the light of the gas was to that of the oil as 21 to 13. Q. What is the ratio of heat?—In experiments made to determine the heat evolved for *equal quantities of light* from oil and gas burning brightly from Argand burners, the heat from the oil being 2, that from the gas was nearly 3. Q. Is either sulphurous or sulphuric acid formed by the combustion of coal-gas in the ordinary way?—A little sulphurous or sulphuric acid is generally formed from the combustion of coal-gas. If well-purified gas be used this product is rarely sensible: it is less sensible as sulphuric than as sulphurous acid. Upon closely questioning persons who have declared they smelt the sulphur from gas, I have usually found they meant something else—generally the oppressive heat, or the dry sensation, or the smell of a little gas unburnt, none of which have anything to do with the sulphur product from gas. Q. From a gas light, properly regulated, does unburned gas escape?—I do not believe that any gas escapes unburnt from a gas light well regulated. It is far more likely that oil vapor should escape unconsumed from an oil burner than gas from a gas burner. Q. Will an oil or gas light soonest soil the ceiling of a room?—Neither oil nor gas ought to soil, or will soil, the ceiling of a room, if well regulated. Either will do so when badly regulated. I think, of the two, oil is most liable to do so; because of the changes which take place in the wick, in the temperature of the oil, &c., during burning, and which do not occur with a gas lamp properly regulated. Q. What are the comparative effects of oil and gas lights on the quality of the air, light for light?—It is exceedingly difficult to ascertain, and, if ascertained, to describe correctly the effects of lights on air, so as to convey a just opinion of their influence; thus, their power of heating is of advantage and desirable up to a certain point, and above that point is unpleasant and disagreeable: but

that point depends upon many other things as well as the lights, and, what is still more important, differs for different persons, so that it becomes impossible to please all. Gas light will heat air faster than oil light; it therefore at first does good quicker, and afterwards does harm quicker than oil. As to the proportionate deterioration of air by the oxygen abstracted, I think it probable that gas would, *light for light*, have the greatest effect; but I do not believe that effect would be sensible in either case. As to the deterioration of air by the sulphurous acid and unburnt gas thrown into the room, I think little of it. Q. What are the comparative qualities of the light from oil and gas?—When the oil was burning in its best manner, still it gave a much yellower flame than the gas; the whiteness of the gas flame is a necessary consequence of its higher temperature. Q. Taking all the circumstances into consideration, what, in your opinion, is the cause of the oppressive feeling complained of in certain rooms in the Athenæum?—In my opinion the principal cause of complaint is of the following nature: a house has been built, and every endeavour made to render floors, ceilings, windows, walls, and doors, tight and close; the rooms in it are well warmed during the day, and are brought to such a temperature and state that the first person who enters is fully satisfied; from fifty to two hundred persons are then introduced, evolving both heat and effluvia; a number of powerful gas burners are next put into and continue in action; and when the injurious agency of these causes is continued for one, two, or three hours, complaints are made that the heat is oppressive, or the odor unpleasant. Things are arranged so as to produce a perfect effect under one set of circumstances, and then, changing the circumstances, the effect is expected to remain the same, though it must of necessity be different. The large room and the library are made quite warm enough by daylight, when there are only a few persons there: then they are lighted, many persons enter, and they must of course very soon expect an oppressive sensation. I have no hesitation in believing that the cause of these complaints might be removed by extending and adjusting the system of ventilation.”

quantity of material consumed by the following candles, which were of the same size and make, and about six to the pound, and occasionally snuffed so as to maintain as nearly as possible an equable flame, was as follows:

	Grains.
Stearic (or composite) candles	164
Cocostearine „	157
Spermaceti „	143
Wax „	134
Tallow moulds „	128

The relative illuminating powers of these candles determined by a shadow photometer, and by Wheatstone’s vibrating reflector, were nearly as follows:

Spermaceti.....	10,000
Stearic	7,463
Wax	6,623
Cocostearine	5,523
Tallow mould	4,784

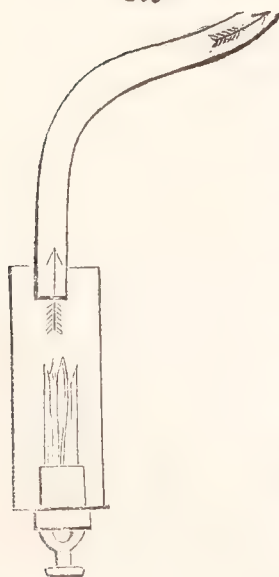
The principal objections to the use of coal-gas illumination, arise out want of due ventilation, by which the products of its combustion, namely, water and carbonic acid, (and almost always traces of sulphurous acid,) may be removed from the apartments: the following details upon this subject are taken from a paper communicated to the Society of Civil Engineers in 1843.

In consequence of the injury sustained by the books in the library of the Athenæum, and the complaints of the vitiated state of the air in the rooms, the attention of Professor Faraday was drawn to the subject of ventilating lamp-burners, and he was induced to suggest the trial of various plans for effecting the removal of the products of combustion produced by sources of artificial light. All substances used for the purpose of illumination may be represented either by oil or by coal-gas; although tallow and wax are also employed, yet as, until rendered fluid like oil, they cannot be burnt, for all practical purposes they may be classed with it. Oil and gas both contain carbon and hydrogen, and it is by the combination of these elements with the oxygen of the air that light is evolved. A pound of oil contains about 0·12 of a pound of hydrogen, 0·78 of carbon, and 0·10 of oxygen; when burnt it produces 1·06 of water, and 2·86 of carbonic acid, and the oxygen it takes from the atmosphere is equal to that contained in 13·27 cubic feet of air. A pound of London coal-gas contains on an average 0·3 of hydrogen, and 0·7 of carbon; it produces, when burnt, 2·7 of water, and 2·56 of carbonic acid gas; consumes 4·26 cubic feet of oxygen, equal to the quantity contained in 19·3 cubical feet of air. A pint of oil (equal in weight to about 13 ounces), when burnt, produces a pint and a quarter of water (weighing 20 ounces.) A pound, or 16 ounces, of coal-gas, produces when burnt, about two pounds and a-half, or 40 ounces of water. A London Argand gas lamp, in a closed shop window, will produce in four hours, two pints and a half of water, to condense or not upon the glass or the goods, according to circumstances. A pound of oil also produces nearly three pounds of carbonic acid, and a pound of gas two and a half pounds of carbonic acid. For every cubical foot of gas burnt, rather more than a cubical foot of carbonic acid is produced. A man breathing in an atmosphere containing

7 or 8 parts of carbonic acid per cent., would suffer, not so much from mere deficiency of oxygen, as from the actual deleterious action of the carbonic acid. Leblanc, who has analyzed the confined air of inhabited places, concludes that the proportion of carbonic acid gas in such places may be regarded as measuring with sufficient exactness the insalubrity of the air; that in the proportion of 1 part to 100 of air, ventilation is indispensable for the prevention of injury to the health; that the proportion of carbonic acid gas had better not exceed a five-hundredth part, though it may rise without inconvenience to a two-hundredth part. If a room twelve feet square and twelve feet high, with the doors, windows, and fire-place, closed, has a gas lamp burning in it, consuming five cubic feet of gas per hour, the light will produce sufficient carbonic acid, in rather more than three hours, to be in the proportion of one part to 100 of air, and, when in such condition, the air is injurious to health: and even in one hour and a half it will produce that proportion of carbonic acid which should never be exceeded. Sulphurous and sulphuric acid are also among results of the combustion of coal-gas, and are products injurious to health and to metals and furniture.

It will now be understood, that the object sought to be attained in the ventilation of lamp-burners is the removal of the products of combustion; and with this view, the gas lights in the library at the Athenæum were ventilated by pipes dipping into the lamp glasses, and conjoining, at a short distance upwards, into one central pipe, which carried away the burnt air.

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In this first practical experiment, many things were learned as to the mode of arranging the pipes; the disposal of the water condensed in them, &c. &c.; but the objects sought for by the ventilation were at once and perfectly obtained. (See fig. 309.)

Then came the desire of modifying the system, by removing the ascending flue from its place over the lamp, not from any deficiency in action, but for appearance sake only; and finding that there was sufficient ascension power in the main part of the metal chimney to allow of a descending draught over the lamp, the tube, in place of going directly upwards, was made to turn short over the edge of the glass, to descend to the arm or bracket, to pass along it, and then ascend at the central part of the chandelier, or against the wall, if applied to a single light. To this succeeded another

form, which appears to be the perfection of lamp ventilation. It is in fact the application of the principle of a descending draught to a lamp-burner*. The gas-light has its glass chimney as usual, but the glass-holder is so constructed as to sustain not merely the chimney, but an outer cylinder of glass larger and taller than the first; the glass-holder has an aperture in it, connected by a mouthpiece with a metal tube which serves as a ventilating flue, and which after passing horizontally to the centre of the chandelier, there ascends to produce draught and carry off the

* To ensure this descending draught, it is often necessary to heat the column of air in the central vertical ventilating tube, which may be done by a small single-jet burner

placed under its lower orifice, and lighted a few minutes before-hand. When the current is once established, this burner may be extinguished.

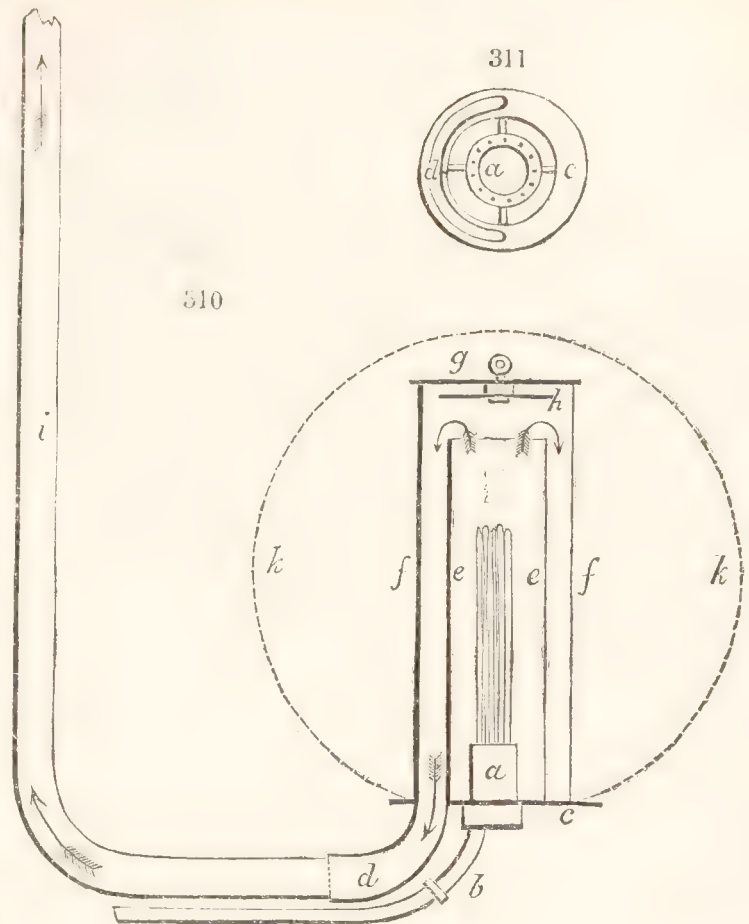
burnt air. Fig. 310, *a*, is the burner; *b*, the gas-pipe leading to the burner; *c*, the glass-holder, with an aperture in it opening into the mouthpiece *d*, which is attached to the metal chimney; *e*, the ordinary glass chimney; *f*, an outer cylinder of glass, closed at the top by a plate of mica, *g*; or, still better, by two plates of mica, one resting on the top of the glass, and the other one, *h*, dropping a short way into it. They are connected by a metal screw and nut, which also keeps them a little apart from each other; thus forming a stopper, which cannot be shaken off the glass chimney, but is easily lifted on and off by the small metal ring or knob at the top: *i*, is

the metallic tube chimney; *k*, a ground globe, which may be applied to the lamp, and which has no opening, except the hole at the bottom, where it rests on the glass-holder; but any other form may be substituted.

Fig. 311, is a plan of the glass holder, showing the burner *a* in the centre, perforated with jets, with openings round it to allow of a free admission of air to the flame—and the aperture, *d*, which opens into the mouthpiece connected with the metal chimney, *i*. The burnt air and results of combustion, take the course indicated by the arrows, and are entirely carried away by the chimney.

Now, with a lamp burning in the ordinary way, the products of combustion issue out as a torrent of aërial impurity into the apartment; but if the above arrangement be applied, on closing the top of the outer glass cylinder by the plate of mica, all smoke, water, carbonic acid, sulphurous and sulphuric acid, and a large portion of the heat, are entirely carried away and discharged into a chimney or the open air. The air in rooms may thus be kept in the same sweet and wholesome condition, and as fit for respiration, as if artificial light were not being used. A curious but important result of the inclosed lamp, is the increase of light produced, amounting to from 10 to 20 per cent., according to circumstances, the same quantity of gas being consumed as before. If the current of air through a lamp glass, when the gas is burning in the usual manner, be diminished, the flame rises in height, and the light is increased in amount; the combustion, in fact, is not so intense, because the access of air is retarded, the particles of carbon which give the light are not so highly ignited, but are more abundant, and are ignited for a longer time, thereby causing an increase of light.

The advantages of this invention are many: it is not objectionable in



architectural appearance; the ventilation is perfect; the heat diminished; the light increased for a given portion of gas; and safety from accidents is obtained, as in the event of leakage from the pipes, or from the gas-cock being left open, the gas would be carried off by the metal tubes.

COAL TAR. From the sketch above given of the composition of coal-gas, and the substances which accompany its evolution, it will appear that they are extremely complicated; they also vary in nature and proportion, according to the circumstances under which they have been evolved. If we consider the principal ultimate elements of common coal as carbon, hydrogen, oxygen, nitrogen, and sulphur, it is obvious that these may give rise to an almost infinite variety of secondary compounds: of these several have been already described in detail, and others will be elsewhere examined. I shall, therefore, conclude this part of our subject with a short account of some compounds not previously mentioned, and which are extracted from *coal tar*.

1. *Carbolic Acid. Hydrate of Phenyle.* The resolution of the oil of coal tar into several distinct products by a graduated distillation has been above adverted to. From that portion of this oil which boils between 300° and 400° , Laurent obtained carbolic acid = $C_{12}H_6O_2$, a compound which it has been found convenient to represent as the hydrated oxide of a radical which has been termed *phenyle*, and of which the assumed formula is $C_{12}H_5$, so that under this aspect carbolic acid would be $C_{12}H_5O + HO$. It is obtained by agitating the oil with about twice its volume of solution of potassa, pouring off the aqueous part, and saturating it by hydrochloric acid: the carbolic acid separates in the form of a heavy oil, which may be purified by cautious distillation off a small quantity of caustic potassa.

Hydrate of oxide of phenyle is a colorless oily liquid, neutral to litmus paper, of a high refractive power, sp. gr. 1.062. It has a penetrating odor, a pungent burning taste, and acts powerfully on the skin: it occasionally assumes the form of acicular crystals which fuse at 94° and boil at 368° . It is slightly soluble in water. It forms crystallizable salts with the alkalis, which, however, retain alkaline reaction. In many of its properties it resembles kreasote. It combines with sulphuric acid to form *sulphocarbolic* or *sulphophenic acid* = $C_{12}H_5O, HO, 2SO_3$, and with chlorine, bromine, and nitric acid, it yields the following substitutional derivations.

Chlorophenesic acid C_{12}	$\begin{matrix} H_3 \\ Cl_2 \end{matrix}$	O,HO
Chlorophenisic acid C_{12}	$\begin{matrix} H_2 \\ Cl_3 \end{matrix}$	O,HO
Bromophenisic acid C_{12}	$\begin{matrix} H_2 \\ Br_3 \end{matrix}$	O,HO
Nitrophenesic acid C_{12}	$\begin{matrix} H_3 \\ 2NO_4 \end{matrix}$	O,HO
Nitrophenisic acid C_{12}	$\begin{matrix} H_2 \\ 3NO_4 \end{matrix}$	O,HO

2. *Kyanol.* 3. *Leucol.* When coal oil is agitated with hydrochloric acid, the mixture separates into an oily stratum above, and an acid solution beneath; the latter is withdrawn and yields, when mixed with excess

of hydrate of lime and distilled, two basic compounds, to which the above names have been applied.

Kyanol, $C_{12}H_7N$, has an agreeable odor and acrid taste: its boiling-point is 358° , its sp. gr. 1.028. Exposed to the air it becomes brown and resinous. It is sparingly soluble in water; soluble in alcohol and ether; neutral to test-paper: dropped into a solution of chloride of lime, it gives a very characteristic *blue* precipitate, which gradually reddens. With sulphuric and oxalic acids it forms crystalline compounds.

Leucol, $C_{18}H_8N$, is less volatile than kyanol; its odor resembles that of bitter almonds; its sp. gr. 1.08. Its compounds with the acids are in general less easily crystallizable than those of kyanol, and it is not rendered blue by chloride of lime.

A substance termed *aniline*, obtained from indigo, and a product found in the empyreumatic oil of bone called *crystallin*, are supposed to be identical in composition with kyanol; and the basic compound obtained by distilling quinia or cinchonia with potassa, termed *quinolein*, has the leading properties of leucol. In short, it is not surprising that similar compounds should in this way be obtained from very dissimilar sources, and we may reasonably expect that one of the results of the progress of organic chemistry will be the artificial production, and identification, so to say, of compounds hitherto considered peculiar and distinct.

CARBON AND NITROGEN. BICARBURET OF NITROGEN. CYANOGEN, NC_2 , or Cy. This gaseous compound was discovered in 1815, by Gay Lussac (*Ann. Ch. et Ph.*, xcv.), and termed *cyanogen* (from *κῡανος*, *blue*, and *γενναω*, *I generate*), in consequence of its being essential to the formation of *Prussian blue*. It is sometimes formed by the direct action of nitrogen upon carbon in the presence of bases (see *Cyanide of Potassium*). It is also formed by heating oxalate of ammonia with about 20 parts of sulphuric acid; but in this case, carbonic acid and carbonic oxide are also evolved.

Pure cyanogen is obtained by heating *cyanide of mercury* in a small retort to dull redness; gaseous cyanogen is evolved, together with the vapor of mercury, and a black substance remains which has been termed *paracyanogen*. Cyanogen is also obtained by heating 6 parts of dried ferrocyanide of potassium and 9 of corrosive sublimate finely pulverised, and well mixed: in this case 1 equivalent of ferrocyanide of potassium and 2 of corrosive sublimate yield 1 equivalent of cyanide of iron, 2 of chloride of potassium, 2 of mercury, and 2 of cyanogen: $FeCy, 2KCy + 2HgCl = FeCy + 2KCl + 2Hg + 2Cy$.

Under a pressure of between three and four atmospheres at the temperature of 45° , Mr. Faraday condensed cyanogen into a limpid colorless liquid, of a specific gravity of about 0.9, and a refractive power rather less than that of water. When a tube containing it was opened, the expansion within appeared inconsiderable, and the liquid slowly evaporated, producing intense cold. It does not conduct electricity. At temperatures below -30° it becomes a transparent crystalline solid. (BUNSEN, *Biblioth. Univer.*, 1839.) The tension of the vapor of liquid cyanogen at 0° is = 1.25 atmospheres; at 32° to 2.37, at 50° to 3.28, at 63° to 4.0, at 70° to 4.5, and at 77° to 5, atmospheres. (FARADAY, *Phil. Trans.*, 1845, 169.)

At common temperatures and pressures, cyanogen is a colorless gas, and has a penetrating and peculiar smell, somewhat resembling that derived from bitter almonds. When a lighted taper is dipped into it, it is immediately extinguished, but the gas takes fire and burns upon the surface in contact with air, with a beautiful and very characteristic rose-colored flame, with blue or purple edges. Its specific gravity to hydrogen is as 26 to 1; and to common air, as 1.82 to 1; 100 cubic inches weigh 55.5 grains, (56.472 grains; TURNER; or at the temperature of 32°, 59.2023 grains; THOMSON.) It sustains a high temperature without decomposition. Water dissolves 4.5 volumes, and alcohol 23 volumes (40 according to Johnston) of this gas. Ether and oil of turpentine also absorb it. The aqueous solution reddens vegetable blues; and, according to Vauquelin (*Ann. Ch. et Ph.*, Oct. 1818), spontaneously decomposes into carbonic and hydrocyanic acids, ammonia, a peculiar acid (which he calls *cyanic*) and a brown substance containing carbon: the ammonia saturates the acids, and the carbonaceous compound is deposited. According to Wöhler (*Ann. Ch. et Ph.*, Lxiii. 73), the mutual action of cyanogen and water is attended by the production of cyanic acid and ammonia, which, by combination, generate *urea*.

Cyanogen may be analyzed by detonation with oxygen, or by passing it over red-hot oxide of copper. One volume, detonated over mercury, with two of oxygen, produces two volumes of carbonic acid and one of nitrogen: showing that cyanogen contains its own volume of nitrogen, combined with carbon sufficient to form two volumes of carbonic acid. It therefore consists of

Carbon.....	2	12	46.1
Nitrogen	1	14	53.9
<hr/>					
Cyanogen....	1		26		100.0

or it may be represented
as annexed:

Carbon.		Carbon.		=	Cyanogen.
6	Nitrogen.	6			
	14				
					26

and the following diagrams show the result of its detonation with oxygen:

Before detonation.

One volume of Cyanogen and two
of Oxygen.

Cyanogen.	Oxygen.
26	16
	Oxygen.
	16

After detonation.

One volume of Nitrogen and two of
Carbonic Acid.

Nitrogen.	Carbonic Acid.
14	22
	Carbonic Acid.
	22

When a mixture of cyanogen and oxygen in these proportions is brought into the contact of a red-hot platinum wire, the temperature pre-

sently rises to whiteness, and a violent explosion ensues; but if the mixture be so far diluted with air as to maintain the wire only at a dull red-heat, the fumes of nitrous acid become abundantly apparent: at common temperatures, spongy platinum does not induce this action.

Iodine, sulphur, and phosphorus, may be sublimed in cyanogen without change; but when they are heated in contact with cyanide of mercury, compounds of those bodies with cyanogen are the result. It also combines with the metals, and constitutes the compounds called *cyanurets* or *cyanides*. The cyanides also combine with each other, and produce an extensive and curious class of salts which have been termed *double cyanides*. As a salifying body, therefore, cyanogen may be compared to chlorine, iodine, &c., for it not only combines, as a simple body would do, with the metals, but also forms a hydracid with hydrogen; in some of its properties it bears an analogy to sulphur.

PARACYANOGEN. CARBURET OF NITROGEN. These terms designate the brown matter which remains in the retort after the preparation of cyanogen from cyanide of mercury, and which, according to Johnston (*BREWSTER'S Journal*, second series, i. 75), is a solid compound of carbon and nitrogen, isomeric with cyanogen. The same compound is produced by the action of mercury on a saturated alcoholic solution of cyanogen, and is also probably formed by charring certain animal substances.

When cyanide of silver is heated in a retort, cyanogen is first given off, and then the residue glows and paracyanogen remains with the metal, forming a grey compound which resists further change by heat; dilute nitric acid abstracts the greater part of the silver and leaves a brown substance, which, when washed, dried, and dissolved in concentrated sulphuric acid affords a brown solution, from which paracyanogen is thrown down by the addition of water. When well washed and dried, it appears as a brown friable substance. (THAULOW.)

Paracyanogen varies in color with the mode of preparation; it is neither fusible nor volatile; it is difficult of combustion in the air; it is soluble in nitric, hydrochloric, and sulphuric acids, and in the caustic and carbonated alkalis. Heated in the air, it first yields half its carbon in the form of carbonic acid, the residue therefore is $\equiv \text{CN}$. Berzelius justly observes, that the properties and combinations of paracyanogen deserve to be attentively studied. (Dr. S. Brown states, that the carbon of paracyanogen is convertible into silicon, *Edinb. Phil. Trans.*, xv. 165, but no other chemist has succeeded in effecting this metamorphosis.)

MELLONE. C_6N_4 . This carburet of nitrogen is one of the products of the destructive distillation of *sulphocyanogen*, under which it will be further described.

CYANOGEN AND OXYGEN. There are three isomeric combinations of cyanogen and oxygen, forming three distinct acids, namely, *cyanic acid* $= \text{CyO}$, which is monobasic; *fulminic acid* $= \text{Cy}_2\text{O}_2$, which is bibasic; and *cyanuric acid* $= \text{Cy}_3\text{O}_3$, which is tribasic.

CYANIC ACID. $\text{C}_2\text{N}_2\text{O}$; or CyO . The existence of this acid was first suspected by Vauquelin in 1818, but the mode of obtaining it and its

properties were first indicated by Wöhler and Liebig. When cyanogen is passed into alkaline solutions, cyanides and cyanates are formed, and so far the action of cyanogen corresponds with that of chlorine, but the extreme tendency of the cyanates so formed to decomposition, prevents their permanent separation. At length, Wöhler succeeded in obtaining a permanent cyanate as follows (*Ann. Ch. et Ph.*, xxvii. 196): 6 parts of ferrocyanide of potassium and 2 of carbonate of potassa, both carefully dried (anhydrous) are intimately mixed in fine powder with 8 parts of pure and dry binocide of manganese: this mixture is heated for some time to dull redness, till a portion dissolved, when cold, in water, does not give a blue precipitate with a persalt of iron. The contents of the crucible are then allowed to cool, reduced to powder, and boiled for 15 minutes in alcohol, sp. gr. 850. The liquid is then filtered hot, and on cooling, it deposits crystals of cyanate of potassa. The alcohol is poured off from the salt and again boiled with the residue, so long as further portions of the cyanate can be thus obtained. When the salt has drained, it is washed with a little strong alcohol, and well dried by pressure in filtering paper and afterwards in vacuo over sulphuric acid: it must be preserved out of contact of air and moisture, otherwise it soon passes into ammonia and carbonate of potassa.

But although the cyanic acid may thus be obtained united to a base, any attempt to set it free by means of another acid is attended by its immediate decomposition into carbonic acid and ammonia. By another process, however, it was isolated in its hydrated state, namely, by subjecting dried *cyanuric acid*, $\text{Cy}_3\text{O}_3, 3\text{HO}$, to distillation, gradually raised to a red heat, when the vapor of the hydrate of cyanic acid is given off and may be condensed in a receiver cooled to 32° . A little sublimed cyanuric acid collects in the neck of the retort, and a peculiar white substance is also formed, which generally renders the product in the receiver turbid.

Hydrate of cyanic acid, CyO, HO , is stated to possess the following singular properties: When its temperature is raised a little above 32° , it becomes an opaque pasty mass, and at length concretes into a porcelain-like indifferent, and insoluble, isomeric substance (*cyamelide*), and this curious change is attended by the evolution of heat, and a series of concussions often amounting to explosions, but without the evolution of any permanent gas. When the acid is retained in ice it undergoes the same change, only more gradually.

This acid in its liquid state is intensely caustic; its odor is penetrating and irritates the eyes and nose: its vapor reddens litmus, it is not inflammable. When diluted with a little water and retained at 32° , its odor is like that of acetic acid, but it soon begins to change, carbonic acid is evolved, carbonate and cyanate of ammonia are formed, and, by evaporation, crystals of urea are obtained. In this case 1 atom of cyanic acid and 3 of water at first yield 1 atom of bicarbonate of ammonia; $\text{C}_2\text{N}, \text{O} + 3\text{HO} = \text{NH}_3, 2\text{CO}_2$: but the cyanic being a stronger acid than the carbonic, the undecomposed cyanic acid combines with the ammonia and expels carbonic acid; and, on evaporation, the cyanate of ammonia combines with an atom of water to form urea. $\text{NH}_4\text{O}, \text{C}_2\text{NO} = \text{C}_2\text{H}_4\text{O}_2\text{N}_2$. (BERZELIUS, *Lehrbuch*. LIEBIG, *Ann. Ch. et Ph.*, xxxiii, 208.)

According to the analysis of Wöhler (*Ann. Ch. et Ph.*, xx. and

xxvii.,) corroborated by the experiments of Liebig, anhydrous cyanic acid consists of

Carbon.....	2	12	35.2	} Cyanogen	1	26	76.47
Nitrogen	1	14	41.1						
Oxygen	1	8	23.7		Oxygen....	1	8
<hr/>	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
Cyanic acid	1.		34		100.0		1		34		100.0

But the anhydrous acid is only known in combination with bases, or with water, as obtained above, or as afforded by the distillation of dry cyanuric acid; in this state it is HO, CyO , containing

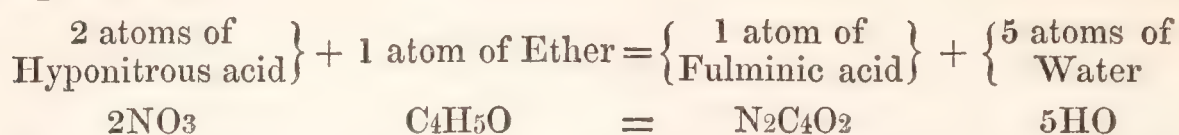
										Liebig.
Carbon	} Cyanogen.....	1	26	60.1	60.23		
Nitrogen										
		Oxygen	1	8	18.6	18.71	
		Water	1	9	21.3	21.06	
<hr/>										
Hydrate of cyanic acid, or	} Cyanate of water.....	1		43		100 0		100.00		
Cyanate of water.....										

CYANATE OF AMMONIA. There are two isomeric cyanates of ammonia. When ammonia and the vapor of hydrated cyanic acid are brought together they combine into a white flocculent and crystallized substance, which, according to Liebig (*Chimie Organique*, i. 126,) contains more ammonia than corresponds with a neutral salt: it is, therefore, apparently a basic salt, but in its properties it agrees with the ordinary cyanates; it is supposed to contain $\text{HO}, \text{CyO}, 2\text{NH}_3$; heated with acids it effervesces, and with alkalis it disengages ammonia; but when gently heated, either in the dry state, or in solution, it gives out ammonia and becomes converted into *urea*, which will be described amongst organic products.

CYANATES. The salts of the cyanic acid are distinguished by the peculiar results of the action of most other acids upon them. If an acid be added to a dry or a dissolved cyanate, effervescence soon ensues, attended by a strong odor of cyanic acid, and if hydrate of lime be then added ammonia is evolved, which it was impossible to detect in the original cyanate. The cyanates of the alkalis are soluble; all the others insoluble. All the soluble cyanates, excepting that of ammonia, are resolved into ammonia and carbonates, when boiled in aqueous solution.

FULMINIC ACID. PARACYANIC ACID. $2\text{C}_2\text{N}_2\text{O}_2$ or Cy_2O_2 . Under the articles *Mercury* and *Silver*, the process for preparing detonating compounds of those metals, by acting upon their nitric solutions by alcohol, is stated: the experiments of Liebig and Gay Lussac (*Ann. Ch. et Ph.*, xxiv. and xxv.) lead to the inference, that in these combinations the metallic oxides are united to an acid containing the same elements, and in the same relative proportions, as the cyanic acid, to which, in that particular state of combination, the term *Fulminic Acid* has been applied; but the equivalent of the fulminic acid is double that of the cyanic, or ≈ 68 . According to Liebig, the results of the action of nitric acid upon alcohol, are hyponitrous acid on the one hand, and on the other, aldehyd, and formic and oxalic acids. In the presence of oxide of mercury or oxide of silver, 2 atoms of hyponitrous acid and 1 atom of ether (the elements of which are contained in the alcohol) become converted into

fulminic acid, which unites to the metallic oxide, as shown in the following equation:—



When the vapor of nitrous acid is passed into a saturated solution of nitrate of silver in alcohol, there is an immediate precipitation of fulminate of silver.

Fulminic acid has not been isolated from the bases with which it is combined; at the moment of its separation by a stronger acid it is resolved into hydrocyanic acid and other products.

If regarded as anhydrous, it consists of

						Liebig.
Cyanogen.....	2	...	52	...	76.47	76.74
Oxygen	2	...	16	...	23.53	23.26
<hr/>						
Fulminic acid	1		68		100.0	100.00

FULMINATES. These are bibasic salts containing either 2 atoms of fixed base (neutral fulminates), or 1 atom of fixed base and 1 atom of water; the latter have an acid reaction. The 2 atoms of fixed base may be represented by 2 atoms of the oxide of an easily reducible metal, or by 2 atoms of the oxides of two different metals, also easily reducible. Thus for example, 2 atoms of oxide of copper, 2 atoms of oxide of silver, 2 atoms of oxide of mercury, or 1 atom of oxide of copper and 1 atom of oxide of silver, may combine with 1 atom of fulminic acid, to form a neutral salt. The fulminates with an alkaline base include 1 atom of easily reducible oxide and 1 atom of alkaline oxide; as, for example, 1 atom of oxide of silver and 1 atom of potassa, baryta, strontia, or oxide of zinc. There are no fulminates of two alkaline bases. When a fulminate of the first class, containing 2 atoms of oxide of silver or of oxide of mercury, is treated by an alkali, only half the oxide is replaced by 1 atom of the alkali. This singular property seems to indicate an intimate relation between the oxygen of the acid and of the oxides with which it combines. (LIEBIG. *Chimie Organique*.)

CYANURIC ACID. $\text{C}_6\text{N}_3\text{O}_3$ or Cy_3O_3 . These elements are only known in combination with 3 atoms of water, or as $3\text{HO} + \text{Cy}_3\text{O}_3$. Scheele first described this acid under the name of *pyrouric acid*; Serullas afterwards obtained it by another process, and termed it *cyanic acid*. (*Ann. Ch. et Ph.*, xxxviii.) Its real nature and properties were first ascertained by Liebig and Wöhler. When urea is heated beyond its fusing point, it evolves ammonia and is converted into a gray substance: if this be dissolved in sulphuric acid, and nitric acid dropped in till the solution becomes colorless, and then added to an equal volume of water, crystals of hydrated cyanuric acid are deposited. Liebig also obtained cyanuric acid from a substance which is produced by the decomposition of the sulphocyanide of ammonium, and which he calls *Melam*. Dry melam is dissolved by a gentle heat in strong sulphuric acid, and then added to 20 parts of water: the mixture is kept near its boiling-point for several days, till it no longer gives a white precipitate with ammonia; it is then evaporated and crystallized. These crystals,

which are rhombic prisms, are composed of 1 atom of the terhydrated cyanuric acid and 4 atoms of water; these they lose by exposure to air, and fall into a white powder, sparingly soluble in water, inodorous, and slightly reddening litmus. It dissolves without decomposition in the strong acids, but by long boiling is converted into carbonic acid and ammonia. The prismatic crystals of cyanuric acid, dried at a temperature of 212° , lose the 4 atoms of water of crystallization, but retain the 3 atoms of combined water; in this latter state of composition the acid may be obtained in flattened octohedra, or oblique quadrilateral prisms, terminated by dihedral summits, by cooling its boiling saturated solution in nitric or hydrochloric acid. The following, therefore, is the composition of the anhydrous cyanuric acid, as it exists in combination with bases, and which cannot be isolated:—

Cyanogen	3	...	78	...	76.47	} = Cy_3O_3
Oxygen	3	...	24	...	23.53	
<hr/> Anhydrous cyanuric acid	<hr/> 1		<hr/> 102		<hr/> 100.0	

The crystallized hydrate (cyanurate of water) consists of

Anhydrous acid	1	...	102	...	79	} = $3\text{HO}, \text{Cy}_3\text{O}_3$
Water (combined)	3	...	27	...	21	
<hr/> Hydrate of cyanuric acid	<hr/> 1		<hr/> 129		<hr/> 100	

And the prismatic crystals contain

Hydrate of cyanuric acid	1	...	129	...	78.2	} = $3\text{HO}, \text{Cy}_3\text{O}_3 + 4\text{HO}$
Water of crystallization	4	...	36	...	21.8	
<hr/> Crystals of cyanuric acid	<hr/> 1		<hr/> 165		<hr/> 100.0	

CYANURATE OF AMMONIA. This salt crystallizes in shining white prisms, efflorescent, and losing ammonia when heated; dried in vacuo it contains the elements of 1 atom of hydrate of cyanuric acid, 1 of ammonia, and 1 of water. (LIEBIG.)

CYANURATES. The cyanuric acid combines with 3 atoms of bases, which are represented by the 3 atoms of water in the hydrate of the acid. This water is either wholly or partially replaced by metallic oxides. The alkaline oxides form two series of cyanurates: in the one, the salt contains 1 atom of anhydrous acid, 1 atom of basic oxide, and 2 atoms of basic water; in the other, 1 atom of acid, 2 atoms of oxide, and 1 of water (as in the corresponding phosphates.) There are no salts constituted of 1 atom of acid with 3 of alkaline oxide. But the cyanurate of silver is anhydrous, and contains 3 atoms of oxide of silver; so that the relative proportion of elements *per cent.* is the same in the *cyanate*, the *fulminate*, and the *cyanurate of silver*, but they differ in the mode of their constitution. All the cyanurates are decomposed by nitric and by hydrochloric acid. The cyanuric acid which crystallizes from a solution of a cyanurate so decomposed, contains no trace of the oxide with which it was combined. The salts with alkaline bases fuse when heated, and leave an alkaline cyanate, whilst cyanate of ammonia, hydrated cyanic acid, carbonic acid, and nitrogen, are evolved. (LIEBIG, *Chimie Organique*.)

CYAMELIDE. INSOLUBLE CYANURIC ACID. The hydrate of cyanuric

acid, when kept for some time, becomes hard and white (like porcelain). In this state it is insoluble in water, dilute acids, alcohol, and ether; it is dissolved and decomposed by caustic alkalis, into ammonia, and alkaline cyanates and cyanurates. Concentrated sulphuric acid, aided by heat, dissolves and decomposes it, resolving it with the addition of 2 atoms of water into carbonic acid and ammonia. Subjected to dry distillation, cyamelide is transformed into hydrate of cyanic acid. These decompositions are intelligible if cyamelide be of the same composition as cyanic acid. (LIEBIG.) The spontaneous transition of cyanic acid into cyamelide has been already noticed.

In the preceding statement we have represented the three oxygen acids of cyanogen as hydrated acids; but they may also be regarded as hydracids; in which case the cyanic acid (monobasic) would be $= \text{CyO}_2 + \text{H}$, the fulminic (bibasic) acid $= \text{Cy}_2\text{O}_4 + \text{H}_2$, and the cyanuric acid (tribasic) $= \text{Cy}_3\text{O}_6 + \text{H}_3$, the hydrogen being in these cases replaceable by a metal, as, in the usual view of their constitution, the water is replaceable by a metallic oxide.

CYANOGEN AND CHLORINE. CHLORIDE OF CYANOGEN. CYANIDE OF CHLORINE. CHLOROCYANIC ACID. $\text{C}_2\text{N}_2\text{Cl}_2$; or CyCl . Gay Lussac procured this compound by passing a current of chlorine through a solution of hydrocyanic acid in water, till the liquid discolored a dilute solution of indigo in sulphuric acid. He then deprived it of excess of chlorine by agitation with mercury, and submitted it to careful distillation, by which an elastic fluid was evolved, consisting of a mixture of carbonic and chlorocyanic acids; and which, when condensed into water, furnished a strong-smelling, colorless solution, which reddens litmus. According to the statement of Liebig, when excess of chlorine is passed into the aqueous solution of hydrocyanic acid, chloride of cyanogen, hydrochloric acid, and free chlorine, are contained in the liquid. When gently heated the chloride of cyanogen is disengaged, and is obtained pure by passing it through a tube containing chloride of calcium. It is gaseous at common temperatures, has an insupportable and pungent odor, and when cooled to 0° crystallizes in long needles, which fuse at 5° and boil at 10° , but under a pressure of about 4 atmospheres remain liquid at 70° . When kept in this state in tubes hermetically sealed, it forms, according to Persoz, white crystals of a solid chloride of cyanogen, having the same composition as the former. Water dissolves 25, ether 50, and alcohol 100 volumes of the gas. It is decomposed by the alkalis. When moist cyanide of mercury is exposed in chlorine to the action of solar rays, a heavy yellow liquid is formed, insoluble in water, and having the odor of chloride of cyanogen; the same substance appears to be formed by the action of chlorine on fulminate of silver.

It appears from the researches of Gay Lussac and Serullas (*Ann. Ch. et Ph.*, xcv. 205), that 100 volumes of the gaseous chloride consist of 50 volumes of cyanogen + 50 volumes of chlorine, the gases combining without change of volume: accordingly, as

	Grains.
50 cubic inches of cyanogen weigh	27·7
50 " chlorine	38·0
<hr/> 100 " chloride of cyanogen should weigh	<hr/> 65·7

and it is a compound of

										Vols.	Sp. Gr.
Carbon	2	12	19.4	} Cyanogen	1	26	42	0.5	0.91		
Nitrogen.....	1	14	22.6								
Chlorine	1	36	58.0		Chlorine	1	36	58	0.5	1.23	
<hr/>											
Chlorocyanic vapor	1	62	100.0		1	62	100	1	2.14		

SOLID CHLORIDE OF CYANOGEN. When a mixture of dry chlorine and anhydrous hydrocyanic acid is exposed to the sun's rays, hydrochloric acid and solid chloride of cyanogen are formed: the latter, when pure, is white, and sublimes in acicular crystals; it has a penetrating odor, resembling that of the excrement of mice; its taste is pungent; its specific gravity 1.32; it fuses at 284° , and sublimes at 374° . When digested in hot water, it is resolved into cyanuric and hydrochloric acids, whereas the gaseous chloride, under the same circumstances, forms cyanic and hydrochloric acids. It is soluble without decomposition in alcohol and ether. According to Bineau 1 volume of the vapor of this compound is constituted of 1.5 of chlorine, and 1.5 cyanogen, so that the 3 volumes are condensed into 1. It combines with ammonia. According to Liebig, this chloride corresponds to cyanuric acid, and is represented by the formula Cy_3Cl_3 .

CHLOROCYANATE OF AMMONIA. One volume of chlorocyanic vapor and two volumes of ammonia condense with slight evolution of heat into white granular crystals, permanent in the air, and inodorous. This salt fuses when heated, and yields ammonia and hydrochlorate of ammonia, leaving a yellow residue, having the characters of *mellone*. (BINEAU, *Ann. Ch. et Ph.*, LXVII. 237, and LXX. 255.)

CYANOGEN AND IODINE. IODIDE OF CYANOGEN. CYANIDE OF IODINE. CyI . This compound was first obtained by Davy (*Quarterly Journal*, i. 289), and afterwards more fully examined by Serullas. (*Ann. Ch. et Ph.*, xxvii.) It may be obtained by heating in a platinum capsule a mixture of 1 part of iodine with 2 of pulverized cyanide of mercury; they speedily react upon each other, and as soon as white fumes arise the capsule may be placed under a dry bell glass; the action goes on, and a volatile white flocculent product is formed. Mitscherlich obtains this compound by distilling the mixture of iodine and cyanide of mercury with a little water, in a retort. It forms acicular crystals of an acrid taste, pungent odor, extremely poisonous, and exciting a flow of tears. It is heavier than sulphuric acid. It dissolves in water, and still more readily in alcohol, and the solutions do not redden litmus: alkaline solutions decompose it, forming iodates and hydrocyanates. It is instantly decomposed by solution of sulphurous acid; iodine is disengaged, and hydrocyanic evolved. Dry sulphurous acid gas does not act upon it. From the experiments of Serullas it is probably composed of

Carbon....	2	12	8.0	} Cyanogen	1	26	17.3	
Nitrogen	1	14	9.3							
Iodine	1	126	82.7		Iodine	1	126
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>	<hr/>
	1		152		100.0		1		152		100.0	

According to Bineau, iodide of cyanogen forms a definite liquid compound with ammonia. (*Ann. Ch. et Ph.*, LXVII. 235.)

CYANOGEN AND BROMINE. BROMIDE OF CYANOGEN. CYANIDE OF BROMINE. CyBr . Two parts of dry cyanide of mercury are put into a small tubulated retort, or into the bottom of a sealed tube, plunged into a freezing mixture: 1 part of bromine is then added; a rapid action ensues, and so much heat is evolved, that if the temperature were not kept down the bromine would be volatilized; bromide of mercury and of cyanogen are formed; the latter crystallizes in needles in the upper part of the tube, whence it may be sublimed into a cold receiver by the application of a gentle heat: sometimes it forms small cubic crystals. In many respects its physical properties resemble those of iodide of cyanogen; its odor is excessively pungent, and it is volatile at temperatures above 60° . It is more soluble in water and alcohol than the compound of iodine. Solution of potassa transforms it into cyanate of potassa and bromide of potassium. The solution furnishes a precipitate when added to nitrate of silver, composed of cyanide and bromide of silver. Like the iodide it is extremely deleterious to animals. One grain of it dissolved in a little water, and introduced into the oesophagus of a rabbit, occasioned almost instant death, as rapidly as hydrocyanic acid; it cannot, therefore, be examined without risk. Its composition has not been accurately determined. (SERULLAS, *Ann. Ch. et Ph.*, vol. xxxiv. p. 100.) It combines with ammonia in two proportions, forming a solid and liquid compound. (BINEAU, *Ann. Ch. et Ph.*, LXX. 257.)

CYANOGEN AND HYDROGEN. CYANIDE OF HYDROGEN. HYDROCYANIC ACID. CYANHYDRIC ACID. PRUSSIC ACID. C_2NH , or HCy . This compound was first obtained by Scheele (*Stockholm Trans.*, 1782, 1783), and its composition ascertained by Berthollet in 1787, and by Clouet (*Ann. Ch. et Ph.*, xi. 30). It was not, however, till the discovery of cyanogen by Gay Lussac, in 1815, that its real nature was understood, and its components accurately determined. Cyanogen and hydrogen have no tendency to direct combination, but by the action of certain acids on metallic cyanides hydrocyanic acid is formed by double decomposition: in this way it is obtained by the action of hydrochloric acid on cyanide of mercury. $\text{HgCy} + \text{HCl} = \text{HgCl} + \text{HCy}$. Introduce the dry and finely pulverized cyanide into a tubulated glass retort, and pour upon it rather less than its weight of hydrochloric acid (sp. gr. 1.20). Adapt a horizontal tube to the beak of the retort, about two feet long and half an inch diameter; fill the first third of the tube next the retort with small pieces of white marble, and the other two-thirds with fragments of fused chloride of calcium; adapt to its extremity a small receiver, surrounded by a freezing mixture; on applying a gentle heat to the retort, hydrocyanic vapor will pass through the tube, and become condensed in the cold receiver; any portion of hydrochloric acid and watery vapor that may arise along with it will be detained by the carbonate and chloride; after this part of the process the whole length of the tube should be gently heated, to expel the residuary hydrocyanic acid. As the extrication of carbonic acid from the marble is not only inconvenient, but liable to carry off hydrocyanic acid, the distillation of any portion of hydrochloric acid should, as far as possible, be prevented, by placing the retort in a horizontal position, using the least possible quantity of it, and employing not more than a sufficient heat. (GAY LUSSAC.) 2. Introduce the dry cyanide of

mercury into a long glass tube terminating at one extremity in a receiver immersed in a freezing mixture, and then, from a proper apparatus, pass over it a stream of pure and dry sulphuretted hydrogen, the sulphur of which combines with the mercury to form sulphuret of mercury, and the hydrogen unites to the cyanogen to form hydrocyanic acid; $\text{HgCy} + \text{HS} = \text{HgS} + \text{HCy}$; the whole of which may be driven, by the application of a gentle heat, into the cold receiver, and there condensed. (VAUQUELIN.)

3. Distil by a gentle heat 15 parts of finely powdered ferrocyanide of potassium, with a mixture of 9 parts of sulphuric acid and 9 of water: the product must be collected in a well cooled receiver containing 5 parts of broken chloride of calcium: the distillation is stopped as soon as the chloride of calcium is covered by the liquid hydrocyanic acid, which is then carefully poured off and preserved in a well-stopped phial. In this process the cyanide of potassium of the ferrocyanide is decomposed by the hydrated sulphuric acid. $\text{KCy} + \text{HO},\text{SO}_3 = \text{KO},\text{SO}_3 + \text{HCy}$. (Cyanide of potassium may be substituted for the ferrocyanide.) TRAUTWEIN.

Anhydrous hydrocyanic acid thus obtained is a limpid liquid of a strong odor, somewhat like that of bitter almonds which have been chewed or triturated with water, and in which, and other species of *amygdalus* and *prunus*, we shall afterwards recognise its formation. Its taste is acrid, and it is highly poisonous, so that the utmost care should be taken to avoid the inhalation of its vapor. It volatilizes so rapidly as to freeze itself, when a drop of it is placed upon a glass plate. Its specific gravity at about 45° is 0.705, and at 64° 0.696; and the specific gravity of its vapor, as experimentally determined by Gay Lussac, is 0.9476: it boils at 80° , and congeals at 3° or 4° above 0° in its ordinary state, but when it is perfectly anhydrous it remains liquid according to Schultz at -40° . It burns with a bright flame. It scarcely affects the blue of litmus. It is very liable to spontaneous decomposition, especially under the influence of light, becoming brown and evolving ammonia, changes which are prevented by the presence of minute portions of other acids. When water is present, the concentrated inorganic acids resolve it into ammonia and formic acid: 4 atoms of water and 1 of hydrocyanic acid, include the elements of 1 atom of formiate of ammonia; $4\text{HO} + \text{C}_2\text{NH} = \text{C}_2\text{H},\text{O}_2; \text{NH}_3, \text{HO}$. It is resolved by chlorine into hydrochloric acid and chloride of cyanogen. The easily reducible oxides (of mercury and silver) decompose hydrocyanic acid, and yield water and a metallic cyanide. When lime or baryta are heated to redness in hydrocyanic vapor, they afford cyanides and cyanates, and hydrogen is evolved.

In the voltaic circuit hydrated hydrocyanic acid appears to yield hydrogen at the negative, and cyanogen at the positive electrode, but the aqueous solution of this acid, when pure, is a very bad conductor of electricity. (See FARADAY'S *Researches*, Series vii., § 771.) When its vapor is mixed with oxygen it may be burned by the electric spark, in which case 2 volumes of hydrocyanic vapor require for perfect combustion 2 volumes and a half of oxygen: the results are water, 2 volumes of carbonic acid, and 1 volume of nitrogen. When potassium is heated in its vapor, cyanide of potassium is formed, and hydrogen, equal to half the volume of the acid, liberated: it appears, therefore, that there is the strictest analogy between the hydrocyanic and the other hydracids, and

that 1 volume of cyanogen and 1 of hydrogen form 2 volumes of the vapor of hydrocyanic acid: and as

50 cubic inches of cyanogen weigh	Grains.
50 " hydrogen	27·74
100 " hydrocyanic acid vapor should weigh	1·06
	28·80

Hydrocyanic acid, therefore, is a compound of

										Vols.	Sp. Gr.					
Carbon	2	...	12	...	44·5	} Cyanogen	1	...	26	...	96·3	...	0·5	...	0·91	
Nitrogen	1	...	14	...	51·8		Hydrogen	1	...	1	...	3·7	...	0·5	...	0·03
Hydrogen	1	...	1	...	3·7											
<hr/>												<hr/>			<hr/>	
Hydrocyanic acid	1		27		100·0		1		27		100		1·		0·94	

HYDRATED HYDROCYANIC ACID. This acid, in various states of dilution, is used in medicine as a sedative, and various processes are resorted to for at once obtaining it at a convenient strength for pharmaceutical purposes. The dilute hydrocyanic acid of the *London Pharmacopœia* is intended to contain 2 per cent. of real acid; that of the *Edinburgh Pharmacopœia* contains 3·2 per cent.; and of the *Dublin Pharmacopœia* only 1·6 per cent. (PEREIRA.) The acid which is sold under the name of *Scheele's acid*, contains 5 per cent., and *Vauquelin's acid* 3 per cent. of real acid. The medicinal hydrocyanic acid sold on the Continent sometimes contains as much as from 10 to 25 per cent. of real acid. A dose of Scheele's acid exceeding 20 drops, and an equivalent portion of any of the other forms of the acid, would generally suffice to destroy life. (TAYLOR, *Manual of Medical Jurisprudence*.)

The process for preparing the dilute hydrocyanic acid of the *London Pharmacopœia*, consists in the decomposition of ferrocyanide of potassium, $\text{FeCy}, 2\text{KCy}$, by dilute sulphuric acid. "Take of ferrocyanide of potassium 2 ounces, sulphuric acid $1\frac{1}{2}$ ounce, water $1\frac{1}{2}$ pint. Mix the acid with four ounces of the water, and to these, when cooled and put into a glass retort, add the ferrocyanide of potassium, first dissolved in half a pint of water. Pour 8 ounces of the water into a cooled receiver, then, having adapted the retort, let 6 fluid ounces of acid, distilled with a gentle heat in a sand bath, pass into this water. Lastly, add 6 more fluid ounces of distilled water, or as much as may be sufficient, that 12·7 grains of nitrate of silver dissolved in distilled water may be accurately saturated by 100 grains of this acid."

This process, as explained by Everett (*Phil. Mag.*, Feb. 1835), consists in the decomposition of 2 equivalents of crystallised ferrocyanide of potassium, $2[\text{FeCy}, 2\text{KCy}, 3\text{HO}]$ by 6 equivalents of oil of vitriol = $6[\text{SO}_3, \text{HO}]$: the products of their mutual reaction being 1 equivalent of biferrocyanide of potassium = $2\text{FeCy}, \text{KCy}$, 3 equivalents of bisulphate of potassa = $3[\text{KO}, 2\text{SO}_3]$ 3 equivalents of hydrocyanic acid = $3[\text{HCy}]$ and 9 equivalents of water = $9[\text{HO}]$.

Another mode of obtaining dilute hydrocyanic acid is to pass sulphuretted hydrogen through water holding in solution a known quantity of cyanide of mercury, so as completely to decompose it; the excess of sulphuretted hydrogen is then abstracted by carbonate of lead, and the solution of hydrocyanic acid filtered: but in this process it is difficult to obtain

a clear and colorless solution without the addition of a drop or two of hydrochloric, or sulphuric acid.

A third process is that suggested by Dr. Clarke, of Glasgow. (THOMSON'S *System*, ii. 220.) In 100 drachms of water dissolve $8\frac{1}{4}$ drachms of *cyanide of potassium*, and add to the solution $18\frac{1}{2}$ drachms of crystallized tartaric acid, previously dissolved in 20 drachms of water. A double decomposition takes place; bitartrate of potassa falls down, and about 120 drachms of water remain, holding in solution $3\frac{3}{8}$ drachms of hydrocyanic acid; or 2·81 *per cent.* of the solution is hydrocyanic acid. A little bitartrate of potassa also remains, which may be avoided by using a little alcohol mixed with the water.

A fourth process recommended by Giese, (TURNER'S *Elements*,) is as follows: 20 drachms of ferrocyanide of potassium are dissolved in 80 of water, and with the solution is mixed a dilute acid made previously with 18 drachms by weight of strong sulphuric acid, and 40 drachms of water, and allowed to cool. The dilute hydrocyanic acid is then distilled off, and if the amount is not 120 drachms, distilled water is added to make up that weight. This is nearly the process of our Pharmacopœia.

Liebig recommends for obtaining dilute hydrocyanic acid the distillation of a mixture of equal parts of cyanide of potassium and sulphuric acid; the cyanide being dissolved in twice its weight of water, and the acid diluted with three times its weight of water: these solutions are to be slowly mixed, and the mixture cautiously distilled. (*Mem. Ch. Soc.*, i. 96.)

As hydrocyanic acid in its dilute state is liable to decomposition, it should be prepared in small quantities and preserved in well-stopped phials out of the presence of light: or a very minute addition of dilute sulphuric or hydrochloric acid may be made to it, by which its tendency to change is prevented.

When dilute hydrocyanic is pure, it leaves no residue on evaporation: *hydrochloric acid* is detected in it by heating it in a water-bath so as to expel the hydrocyanic acid, and then testing by sulphate of silver; or the sulphate of silver may be added at once to the hydrocyanic acid and the mixed chloride and cyanide of silver, digested in hot nitric acid, which takes up the cyanide, forming with it a somewhat turbid solution, but leaves the chloride untouched: if *sulphuric acid* be present, it occasions a precipitate on adding nitrate of baryta, which is insoluble in nitric acid. Its odor of course varies in intensity with the state of dilution, of which, however, it is no safe criterion, different persons, and even the same person at different times, being in this respect very differently susceptible.

However carefully the dilute hydrocyanic acid may have been prepared, its real strength must always be determined by a separate experiment, for the specific gravity is no adequate criterion. Dr. Ure proceeds as follows: To 100 grains, or any other convenient quantity of the acid, contained in a small phial, add, in succession, small quantities of pure peroxide of mercury in very fine powder, till it ceases to be dissolved on agitation: the weight of the oxide taken up, being divided by 4, gives a quotient representing the quantity of real acid present. By weighing out beforehand, on a watch-glass, 40 or 50 grains of the peroxide, the residual weight of it shows at once the quantity expended. (*Quarterly Journal*, xiii. 312.) Dr. Ure's *Essay* also contains a table of the specific

gravity of the acid of various degrees of dilution, and directions for detecting the presence of hydrochloric acid in it. The strength of the medicinal acid may also be determined by precipitation by nitrate of silver, which throws down an insoluble cyanide of silver, of which 134 parts are equivalent to 27 of anhydrous hydrocyanic acid; so that if the weight of the precipitated cyanide of silver (well washed, and carefully and perfectly dried,) be divided by 5, the product will almost exactly represent the quantity of real acid.

The virulently poisonous nature of this acid has led to its occasional administration with criminal intentions: the mode in which it produces death, and the symptoms, are enumerated by medical and physiological writers, but the chemist may be called upon to suggest means of detecting it: this may often be effected in consequence of its peculiar odor; and if the fluid containing it be agitated with finely-powdered peroxide of mercury, crystals of cyanide of mercury may be obtained on evaporation. The following is an accurate test of its presence, originally suggested by Scheele: to the suspected liquid add a solution of *protosulphate* of iron, and afterwards drop in pure potassa in slight excess, and after a short exposure to the air, redissolve the precipitate in hydrochloric acid. If hydrocyanic acid be present, the tint of Prussian blue will appear. Except, however, in cases of recent examination, it is not always easy to detect hydrocyanic acid in the contents of the stomach after death, more especially where putrefaction has gone to any extent: in such cases Leuret and Lassaigne have recommended the following procedure: The stomach and its contents, cut into pieces, are carefully distilled with water slightly acidulated by sulphuric acid: the volatile products are condensed in a receiver surrounded by ice, and examined by the above-mentioned methods, or by the formation of cyanide of silver: in such cases the acid is also generally recognizable by its odor. When hydrocyanic acid is present in liquids, the color and composition of which prevent its detection by the formation of Prussian blue, and which interfere by their own odors with that of the acid, it may frequently be detected, and even in minute quantities, by the action of its vapor upon nitrate of silver: thus, if the suspected liquid be placed in a shallow capsule or watch-glass, with another, moistened with nitrate of silver, immediately above it, the nitrate will soon be rendered milky by the formation of cyanide of silver; a few drops of the pharmaceutical hydrocyanic acid added to tea or to porter, are detectable in this way, and may be identified either by collecting and heating the cyanide of silver in a very small tube, so as to evolve cyanogen; or by acting upon it by a few drops of solution of caustic potassa, which generally dissolves it, and then using sulphate of iron and a little hydrochloric acid, so as to form Prussian blue. (See *Cyanide of Silver*.)

Ammonia, and chlorine, are said to be the most effective antidotes in cases of poisoning by hydrocyanic acid: a mixture of protoxide and peroxide of iron and an alkali, so as to form Prussian blue, has also been recommended by Messrs. Smith. (*Pharm. Journ.*, v. 38.) Ten grains of protosulphate of iron, and a drachm of tincture of sesquichloride of iron, dissolved in an ounce of water, and 20 grains of carbonate of potassa in 2 ounces of water, are the proportions which they suggest. In most cases, however, no antidote can be expected to be successful, in consequence of

the rapid action of the poison, which usually proves fatal in a few minutes: cold affusion upon the region of the spine has been especially recommended; but for its toxicological history I must refer to writers on that subject. (CHRISTISON, *On Poisons*. PEREIRA, *Elements of Mat. Med.* TAYLOR, *Medical Jurisprudence*.)

HYDROCYANATE OF AMMONIA. CYANIDE OF AMMONIUM. This salt may be obtained by the action of gaseous ammonia upon anhydrous hydrocyanic acid: it crystallizes in cubes or small prisms, and is extremely volatile. Bineau obtained it by heating equivalents of cyanide of mercury, or of dried ferrocyanide of potassium, with sal ammoniac. (*Ann. Ch. et Ph.*, LXVII. 231.) Dr. Thomson states, that when Prussian blue is exposed to a red heat, and the products of its decomposition received over mercury, the glass receiver becomes coated with crystals of this salt. It soon suffers spontaneous change when dissolved in water, and is decomposed by carbonic and other feeble acids. From Bineau's experiments it appears to consist of 17 ammonia + 27 hydrocyanic acid, elements which upon the ammonium theory are equivalent to $\text{NH}_4 + \text{Cy}$: its empyric formula being $\text{C}_2\text{H}_4\text{N}_2$. According to Langlois, (*Ann. Ch. et Ph.*, I. 111,) cyanide of ammonium is also formed by passing ammonia over red-hot charcoal.

CYANOGEN AND SULPHUR. SULPHOCYANOGEN. CYANIDE OF SULPHUR. CyS_2 . Sir H. Davy obtained this compound in 1816, by heating a mixture of sulphur and cyanide of mercury. (*Quart. Jour.*, i. 289.) Liebig obtains it by saturating a concentrated solution of sulphocyanide of potassium with chlorine, or by boiling a soluble metallic sulphocyanide in dilute nitric acid; it falls in the form of a yellow precipitate, which preserves its color when dry, and is insoluble in water, alcohol, and ether, but soluble in hot sulphuric acid, from which it is again thrown down by water. It is decomposed by concentrated nitric acid: when heated with potassium, sulphuret, cyanide, and sulphocyanide of potassium are formed: subjected to dry distillation, it yields carburet of sulphur, and ultimately nitrogen and cyanogen. (LIEBIG.) By digesting cyanide of mercury in chloride of sulphur, Lassaigne obtained a compound in brilliant crystals, which he regarded as containing 4 atoms of cyanogen and 1 of sulphur (*Ann. Ch. et Ph.*, xxxix.), but which, according to Liebig, are a compound of chloride of cyanogen with chloride of sulphur. The elements of sulphocyanogen* are

Carbon	2	...	12	...	20·7	} Cyanogen	1	...	26	...	44·8
Nitrogen	1	...	14	...	24·1						
Sulphur	2	...	32	...	55·2		Sulphur	2	...	32	...
<hr/>											
Sulphocyanogen....	1		58		100·0		1		58		100·0

MELLONE. When dry sulphocyanogen is heated, sulphur and sulphuret of carbon are evolved, and a yellow substance remains, discovered

* According to Parnell sulphocyanogen, though it exists in combination with bases, has not been isolated: the above yellow substance always containing hydrogen and oxygen, and having the formula $\text{C}_{12}\text{H}_3\text{N}_6\text{S}_{12}\text{O}$. (See *Sulphocyanide of Potassium*.)

and analysed by Liebig; it is represented by C_6N_4 , and possesses, like cyanogen, the properties of a salt-radical, combining with hydrogen and the metals: it is insoluble in water, dilute acids, and alcohol: it bears a dull red heat without decomposition, but when strongly ignited is resolved into 3 volumes of cyanogen, and 1 of nitrogen. It combines directly with potassium, producing ignition; the result is *mellonide of potassium*, which is also formed when mellone is heated with iodide, bromide, or sulphocyanide of potassium, iodine, bromine, and sulphocyanogen being expelled. (LIEBIG.) When mellonide of potassium is dissolved in boiling water and decomposed by hydrochloric, nitric, or sulphuric acid, a white gelatinous substance falls, which is a hydrate of *hydromellonic acid*: $C_6N_4H + HO$: it dries into a yellow powder, and is not decomposed by hydrochloric or nitric acid. (L. GMELIN.)

Liebig.				Gmelin.			
Carbon....	6	36	39.13	Mellone.....	1	92	98.9
Nitrogen	4	56	60.87	Hydrogen.....	1	1	1.1
<hr/>				<hr/>			
Mellone....	1	92	100.00	Hydromellonic acid	1	93	100.0

Mellone is decomposed by the continued action of boiling nitric acid; the action is attended by the disengagement of gas, and the solution deposits on evaporation colorless and anhydrous octohedral crystals. On dissolving these crystals in boiling water, the solution yields pearly flakes on cooling, which retain a certain quantity of water. The crystals are similar in composition to the cyanuric acid, with which they may be said to be isomeric; their formula according to Liebig being (when anhydrous) Cy_6O_6 .

CYANOGEN, SULPHUR, AND HYDROGEN. By mixing cyanogen and sulphuretted hydrogen, Gay Lussac obtained a yellow crystallized compound. (*Ann. Ch. et Ph.*, xcv.) This probably consists of one atom of cyanogen, and one of sulphuretted hydrogen, and is identical with the compound obtained by passing sulphuretted hydrogen into a saturated alcoholic solution of cyanogen. The mutual action, however, of cyanogen and sulphuretted hydrogen requires to be more minutely examined. We are indebted to Porrett (*Phil. Trans.*, 1814), for our knowledge of a triple compound of cyanogen, sulphur, and hydrogen, which he termed *sulphuretted chyazic acid*, but the term *sulphocyanic acid*, or *hydrosulphocyanic acid*, is now generally applied to it.

SULPHOCYANIC ACID. HYDROSULPHOCYANIC ACID. SULFOCYANHYDRIC ACID. RHODANIC ACID. CyS_2H . This acid is obtained, according to Rink, by decomposing basic sulphocyanide of lead by dilute sulphuric acid, taking care to leave excess of lead, which is afterwards removed by sulphuretted hydrogen. It is also formed when sulphocyanide of lead or silver diffused through water is decomposed by sulphuretted hydrogen.

Hydrosulphocyanic acid is colorless, easily decomposed by exposure to air or heat, yielding among other products a peculiar yellow insoluble powder (Mellone): chlorine and nitric acid abstract its hydrogen, and evolve sulphocyanogen; by their prolonged action cyanic and sulphuric

acids are formed, and ultimately ammonia. It reddens the solutions of persalts of iron, (hence called by Berzelius *Rhodanic acid*); it is not poisonous; it exists in the seeds of the cruciferous plants, and in human saliva, and that of the sheep. It has not been isolated in an anhydrous state. From the experiments of Porrett (*Ann. of Phil.*, xiii.), confirmed by Berzelius, its elements are

Berzelius.									
Carbon	2	12	20·3	20·30	Sulphocyanogen 1 58 98·32				
Nitrogen	1	14	23·7	23·85					
Sulphur	2	32	54·2	54·17					
Hydrogen	1	1	1·8	1·68	Hydrogen	1	1	1·68	
<hr/>									
Hydrosulpho- cyanic acid }	1	59	100·	100·00		1	59	100·00	

HYDROPERSULPHOCYANIC ACID. CyS_3H , is a compound described by Liebig, (on the authority of Woskresensky,) as obtained by fusing sulphocyanide of potassium in a stream of dry hydrochloric acid gas; hydrosulphocyanic acid is liberated and immediately decomposed into sulphuret of carbon, hydrocyanic acid, and a yellow product insoluble in water. If this operation be conducted in a retort, a quantity of the yellow product lines the neck of it; it is soluble in boiling alcohol, and precipitates on cooling in the form of a pale yellow crystalline powder sparingly soluble in water: it dissolves in the alkalis, and forms peculiar combinations with the other metallic oxides which are in general insoluble.

SULPHOCYANIDE OF AMMONIUM. HYDROSULPHOCYANATE OF AMMONIA. $\text{CyS}_2 + \text{NH}_4$, or $\text{HCyS}_2 + \text{NH}_3$. This salt is obtained by saturating ammonia with hydrosulphocyanic acid, and evaporating in vacuo. It is also formed by the mutual action of sulphuret of carbon and alcohol saturated with ammonia. It is decomposed by heat, giving off ammonia, sulphuret of carbon, and carbosulphuret of ammonium; and if not too highly heated, the residue consists of mellone and melam.

MELAM. $\text{C}_{12}\text{N}_{11}\text{H}_9$. When sulphocyanide of ammonium, or a mixture of 2 parts of sal-ammoniac and 1 of sulphocyanide of potassium, are heated up to the fusing-point of the latter, one solid and three volatile products are obtained; the latter are ammonia, sulphuretted hydrogen, and sulphuret of carbon; the solid body is melam, mixed with chloride of potassium, which may be removed by washing with water.

Melam is a whitish-gray powder, insoluble in water, alcohol, and ether. It is dissolved and decomposed by long boiling in solution of potassa. Boiling nitric and sulphuric acids dissolve it, and their solutions treated by alcohol produce a precipitate of *ammelide*; but if boiled for several hours, with the occasional addition of water, the melam is wholly transmuted into cyanuric acid and ammonia. Melam is soluble in dilute hydrochloric and nitric acid, and converted into *ammeline* and *melamine*; the same products are obtained by continued boiling in solution of caustic potassa. When fused with hydrate of potassa, it is transformed into cyanate of potassa and gaseous ammonia. By the action of heat it is resolved into mellone and ammonia.

To the above statement, Liebig adds the following explanatory equations :

The ultimate elements of 8 atoms
of sulphocyanide of ammonium } $C_{16} \quad N_{16} \quad H_{32} \quad S_{16}$
 $8[CyS_2 + NH_4]$ are

These are resolved by heat into

1 atom of melam	C_{12}	N_{11}	H_9	
5 „ of ammonia		N_5	H_{15}	
4 „ bisulphuret of carbon	C_4			S_8
8 „ sulphuretted hydrogen.....			H_8	S_8
	C_{16}	N_{16}	H_{32}	S_{16}

And as regards the conversion of 1 atom of melam and 6 of hydrate of potassa into 6 atoms of cyanate of potassa and 5 of ammonia,

The ultimate elements of 1 atom of melam are	C_{12}	N_{11}	H_9	
6 atoms of hydrate of potassa			H_6	$O_{12} \quad K_6$
	C_{13}	N_{11}	H_{15}	$O_{12} \quad K_6$

Resolved by fusion into

6 atoms of cyanate of potassa	C_{12}	N_6		O_{12}	K_6
5 „ ammonia		N_5	H_{15}		
	C_{12}	N_{11}	H_{15}	O_{12}	K_6

MELAMIN. $C_6N_6H_6$. Liebig thus designates a salifiable base, produced as above stated by the action of alkalis and dilute acids on melam : it is one of the most highly azotised compounds with which we are acquainted. To obtain it, melam (procured by the distillation of a mixture of 1 part of sulphocyanide of potassium, and 2 of sal-ammoniac, and washed to free it from chloride of potassium) is boiled in a solution of 1 part of hydrate of potassa in 20 of water, till the turbid liquor becomes clear ; it is then evaporated by a gentle heat, till small brilliant crystals form in it when it is set aside, and on cooling the whole of the melamin separates. It is purified by recrystallization.

Melamin forms anhydrous rhomboidal octohedra, transparent and colorless, or slightly yellow : very sparingly soluble in cold water, and more soluble, but slowly so, in hot water. It is insoluble in alcohol and in ether. Its aqueous solution has a bitter taste, and is without action upon vegetable colors. Dry melamin fuses at a high temperature, and sublimes almost without decomposition ; a small portion of it is, however, resolved into mellone and ammonia.

Concentrated nitric and sulphuric acids decompose melamin with the aid of heat into ammonia and ammelide or ammeline. Fused with hydrate of potassa, the elements of 3 atoms of water combine with it, and transform it into 3 atoms of ammonia which escape, and 3 atoms of cyanic acid which remain in combination with the potassa.

The ultimate elements of 1 atom of melamin are	C_6	N_6	H_6	
3 atoms of hydrate of potassa			H_3	$O_6 \quad K_3$
	C_6	N_6	H_9	$O_6 \quad K_3$

Resolved by fusion into

3 atoms of cyanate of potassa	C_6	N_3		O_6	K_3
3 „ ammonia		N_3	H_9		
	C_6	N_6	H_9	O_6	K_3

Melamin combines with dilute acids to form crystallizable salts, all of which, except the double salts, have an acid reaction. The nitrate, phosphate, and oxalate, are less soluble than melamin; the acetate and formiate are very soluble: it precipitates a part of magnesia from its solutions, and forms a double salt with the residue; in the same way it decomposes the salts of all the common metals. It combines directly with the anhydrous hydracids. All the salts of melamin with the oxyacids, contain an atom of water, like the corresponding salts of ammonia, and cannot exist without it. It forms double basic salts in which this atom of water is replaced by an equivalent of metallic oxide.

AMMELIN. $C_6N_5H_5O_2$. A product of the decomposition of melam and melamin by acids and alkalis. When melamin is prepared by decomposing melam by a solution of caustic potassa, a liquor is obtained, which, after having deposited the whole of the melamin which it held in solution, still retains ammeline dissolved by the potassa, which is thrown down in the form of a white gelatinous precipitate by acetic acid. This precipitate is to be washed and re-dissolved in dilute nitric acid. This nitric solution yields, by evaporation, crystals of pure nitrate of ammeline. These crystals are again dissolved in dilute nitric acid, and from this solution carbonate of ammonia throws down perfectly pure ammeline, which may be washed and dried.

Ammelin may also be obtained by dissolving melam in weak and boiling hydrochloric acid; by evaporation crystals of hydrochlorate of ammeline and of melamin are obtained, which are to be re-dissolved in boiling water; from this solution ammeline is thrown down by caustic ammonia, and the remaining liquid yields crystals of hydrochlorate of melamin.

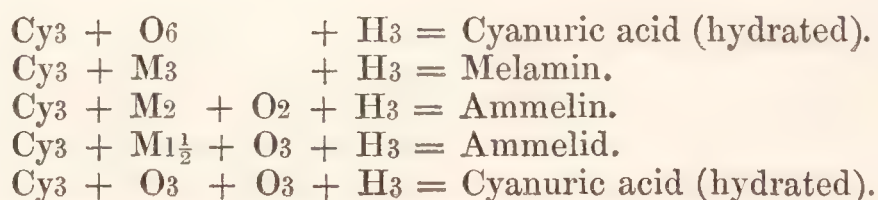
The precipitated ammeline forms brilliant white silky needles; it is insoluble in water, alcohol, and ether, but it dissolves in the caustic alkalis. Subjected to dry distillation, it affords a crystalline sublimate, ammonia, and a residue of pure mellone. With the acids it yields crystallizable salts. By the prolonged action of weak boiling acids, and of concentrated sulphuric acid, it is changed by the assumption of the elements of 1 atom of water: the products of this change are ammonia and ammelid. Fused with hydrate of potassa, it is transformed into ammonia and cyanate of potassa.

Ammelin is a very weak base, and only combines with the stronger acids, and never with the organic acids; its salts are crystalline, have an acid reaction, and are decomposed by water, which separates ammeline. On mixing nitrate of ammeline with the salts of many of the common metals, crystalline precipitates are formed, which are double basic salts, containing 1 atom of acid, 1 of ammeline, and 1 of metallic oxide. The oxyacid salts of ammeline contain, like the salts of ammonia, 1 atom of water; the double basic salts are anhydrous. Nitrate of ammeline crystallizes in large broad plates, or in long quadrangular prisms: it fuses when heated, and leaves ammelid as a residue, while nitric acid, and the products of the decomposition of nitrate of ammonia, are evolved.

AMMELID. $C_{12}N_9H_9O_6$. A product of the decomposition of melam and ammeline by the concentrated acids: either of these is dissolved in

concentrated sulphuric acid, the solution mixed with alcohol, and the precipitate formed washed with cold water till all traces of acid are removed. It is purified by dissolving it in dilute nitric acid, and precipitating by carbonate of ammonia. Ammelid is a white powder, insoluble in water, alcohol, and ether; but soluble in alkalis and strong acids. With nitric acid it forms crystals which are decomposed by water. Exposed to the prolonged action of boiling dilute nitric or sulphuric acid, it is entirely resolved into ammonia and cyanuric acid. On adding slight excess of nitrate of silver to a boiling solution of ammelid in dilute nitric acid, and then ammonia till it forms a constant precipitate, white caseous flocculi are deposited on cooling, consisting of ammelid, in which the elements of an atom of water are replaced by those of oxide of silver.

THEORY OF THE COMPOSITION OF MELAMIN, AMMELIN, AND AMMELID. In the following table, Liebig attempts to explain the basic properties of melamin and ammelin, and the manner in which ammelid and cyanuric acid are derived from them. It is assumed that these substances contain the same radical as cyanuric acid, namely, $C_6N_3[=3Cy]$ together with a compound of equal volumes or atoms of nitrogen and hydrogen, NH , which may be represented by M : in this case the formulæ will stand as follows :



The hydrate of cyanuric acid forms the beginning and end of the series. In melamin 6 atoms of oxygen are replaced by $3M$, and in ammelin 4 atoms by $2M$: both of these are saline bases; ammelid possesses no basic properties, and in it half the oxygen of the cyanuric acid is replaced by $1\frac{1}{2}M$; lastly, when the whole of M is replaced by oxygen, the cyanuric acid again appears. The basic properties of these substances diminish, in proportion as the oxygen of the radical increases. Liebig says that the cyanuric acid may be compared to the phosphoric acid, and melamin to ammonia (or to phosphuret of hydrogen); inasmuch as ammonia and melamin combine directly with the hydracids; that is, without the intervention of water; but with the oxyacids an atom of water enters into the compound, where it plays the same part as in the salts of ammonia.

CYANIDE OF SELENIUM. No binary compound of cyanogen and selenium has been obtained; but by fusing selenium with ferrocyanide of potassium, a compound is formed analogous to that of sulphur: the *hydro-seleniocyanic acid* has, however, not been separated, so that its existence is as yet hypothetical.

CARBON AND SULPHUR. BISULPHURET OF CARBON. CS_2 . This compound was first obtained in 1796 by Lampadius, while distilling a mixture of pyrites and charcoal, and he termed it *alcohol of sulphur*. It was long regarded as a triple compound of carbon, sulphur, and hydrogen, till Clement and Desormes (*Ann. de Chim.*, xlii.), and Cluzel (*Ann. de Chim.*, lxxxiv.), showed the absence of hydrogen; its properties and composition

were afterwards more accurately determined by Marcet and Berzelius. (*Phil. Trans.*, 1813, p. 171.) It is obtained by passing the vapor of sulphur over red-hot charcoal in a porcelain tube; or by distilling about six parts of yellow iron pyrites (bisulphuret of iron) with one of charcoal. Several forms of apparatus have been suggested for this purpose. (GMELIN, *Handbuch*.) One of the most effective appears to be that described by Schrötter. (*Ann. der Pharm.*, xxxix. 297.) The charcoal should be in small fragments and at a high red heat, the sulphur vapor slowly passed through it, and the refrigerator and receiver should be cooled to 32° , or lower; porcelain and coated earthenware vessels answer best, though it is difficult to prevent loss by the escape of the vapor; iron, at the high temperature which is required, too easily combines with the sulphur to render it conveniently available. The product is sometimes conveyed by a glass tube into ice-cold water. When purified by redistillation at a low temperature with chloride of calcium, it is transparent, colorless, and insoluble in water, but soluble in alcohol and ether; its refractive power in regard to light is very considerable. Its specific gravity is 1.272. It boils at 106° , and does not freeze at -60° . It is very volatile and inflammable, and has a pungent taste and peculiar fetid odor. The cold which it produces during evaporation is so intense, that by exposing a thermometer-bulb, covered with fine lint, and moistened with it, in the receiver of an air-pump, the temperature sunk, after exhaustion, to -80° . When a mercurial thermometer was used, the metal froze. It is soluble in fixed and volatile oils, and it dissolves camphor. It is decomposed, when water is present, by chlorine and iodine; and when potassium is heated in its vapor it burns and decomposes it. It dissolves sulphur and phosphorus, and the solution often deposits those substances in beautiful crystals. This solution of phosphorus is occasionally used to give a thin film of phosphorus to delicate articles intended to be coated with metals: they are dipped into it, and then into a solution of silver or copper, by which a film of the metal is reduced upon the surface: upon this, other metals may be precipitated by voltaic powers. When a piece of paper is dipped into this solution, the sulphuret of carbon soon evaporates upon exposure, and a film of phosphorus remains upon the paper, which generally inflames spontaneously: the solution is a powerful and often useful deoxidizer. The readiness with which phosphorus dissolves in the bisulphuret of carbon is remarkable, and the amount considerable, 1 part of the bisulphuret taking up from 8 to 10 (according to Böttger 20,) parts of phosphorus. When the vapor of bisulphuret of carbon is passed over heated lime or baryta, it produces ignition, and carbonates of those bases, together with sulphurets of calcium and of barium. It is also decomposed by copper and iron at a red heat. Nitrohydrochloric acid converts bisulphuret of carbon into a crystalline compound of carbon, sulphur, chlorine, and oxygen. (BERZELIUS.) Under the influence of dry chlorine it yields chloride of sulphur and perchloride of carbon. (KOLBE, *Ann. der Chem. und Pharm.*, Feb. 1843.)

Bisulphuret of carbon appears to be frequently formed during the production of inflammable gas from coal, and to be retained in the state of vapor by the gas after its purification by lime; such gas gives a sulphurous smell when burned, although perfectly cleansed from sulphuretted hydrogen, so as not to discolor carbonate of lead. (*Phil. Trans.*, 1820,

p. 19.) When its vapor is burned with oxygen it forms carbonic and sulphurous acid. It consists of

					Berthollet, Thenard, and Vauquelin.	Berzelius and Marcet.
Carbon	1 6	15.79 14 15.17
Sulphur	2 32	84.21 86 84.83
<hr/>						
Bisulphuret of carbon	1 38	100.00 100 100.00

According to Mitscherlich, (who has also described an apparatus for obtaining sulphuret of carbon upon a large scale, *Lehrbuch*, i. 153,) the specific gravity of the vapor of this compound is 2.640, and one volume of it is composed of one-third of a volume of sulphur vapor = $\frac{6.654}{3} = 2.218$, and half a volume of carbon vapor = $\frac{0.8438}{2} = 0.4219$.

The charcoal which remains in the tube or vessel employed in making the bisulphuret of carbon, retains a portion of sulphur with great obstinacy, and in some peculiar state of union, retaining it at very high temperatures, and only allowing of its separation by slow combustion: it is perhaps a *supercarburet of sulphur*; and it seems not improbable that the sulphur of pit coal is in this state of combination. According to Proust, the same compound is formed when the residue of lixiviated gunpowder is heated.

HYDROXANTHIC ACID. CARBOSULPHURIC ACID. According to Zeise, carbon and sulphur form a base acidifiable by hydrogen, which he has called *Xanthogene*, from the yellow color of its compounds: the acid he terms *hydroxanthic acid*. When an alcoholic solution of pure potassa is mixed with bisulphuret of carbon, a compound is obtained, which, evaporated under the exhausted receiver of the air-pump over a surface of sulphuric acid, or exposed to a temperature of 32°, deposits acicular crystals, which become yellow by exposure to air, are very soluble, and from which upon the addition of dilute hydrochloric or sulphuric acid, an oily-looking fluid, heavier than water, is separated, which is the *hydroxanthic acid*. Exposed to air it becomes covered with an opaque crust: it reddens litmus; tastes sour, astringent, and bitter; is inflammable; and at 212° is decomposed into bisulphuret of carbon and an inflammable gas. The action of ammonia on the sulphuret of carbon is very peculiar, and several new compounds result; but upon these subjects the reader must consult the original sources of information, which scarcely admit of abridgement, and are not very perspicuous in their details. (*Ann. Ch. et Ph.*, xxi. and xxvi.; *Annals of Phil.*, N. S., iv.; *Quart. Journal*, xviii.) Berzelius regards bisulphuret of carbon as a *sulphur acid*, and as forming in combination with certain metallic sulphurets, or *sulphur bases*, a distinct class of *sulphur salts*. According to Couerbe (*Ann. Ch. et Ph.*, lxi. 225), hydroxanthic acid is a *hydrated carbosulphate of oxide of ethyle*, (or a carbosulphate of alcohol) = $C_4H_5O, HO, + 2CS_2$. (See *Ethers*.)

CARBON AND PHOSPHORUS. PHOSPHURET OF CARBON. To obtain this compound, Dr. Thomson directs the following process (*System*, ii. 259): Allow common phosphuret of lime to remain in water till it no longer evolves gas: then add to the liquid excess of hydrochloric acid, agitate for a few moments, and throw the whole upon a filter; phosphuret of carbon remains, which is to be washed and dried. This compound is a soft

powder, of a yellowish color, without taste or smell: exposed to air, it slowly imbibes moisture, and acquires an acid flavor. Exposed to a red heat, it burns, and gradually gives out its phosphorus, the charcoal being prevented burning by a coating of phosphoric acid. It consists of phosphorus 0.62 + carbon 0.38. (THOMSON'S *Annals*, viii. 157.) It would appear from the mode of obtaining this phosphuret, that it forms an ingredient in phosphuret of lime, as usually prepared; it also is formed in the process for procuring phosphorus, and exists in the red matter which contaminates phosphorus when first distilled.

CARBON AND SELENIUM. CARBBURET OF SELENIUM. SELENIURET OF CARBON. Berzelius has announced the existence of this compound, but has not described its properties. (*Lehrbuch der Chemie*, Dresden, 1844, p. 220.)

§ XII. BORON. B. 11.

THIS substance was discovered in 1807, by Sir H. Davy, and in 1808 its properties were examined by Gay Lussac and Thenard. (*Recherches Physico-Chimiques*.) It is obtained by heating in a copper tube two parts of potassium, with one of boracic acid previously fused and powdered. The fused matter is washed out of the tube with water, and the whole put upon a filter. The boron remains in the form of a brown insipid insoluble powder. According to Döbereiner (*Ann. Ch. et Ph.*, ii. 214), one part of charcoal or lamp black, intensely heated in a gun-barrel, with nine parts of borax, previously fused, and in fine powder, produces a disengagement of carbonic oxide, and a blackish mass results, which, after copious washings in boiling water, and once with hydrochloric acid, affords a greenish-black powder, having the characters of boron mixed with a little charcoal. The charcoal probably first reduces the soda, and the sodium decomposes the boracic acid; hence the produce of boron would probably be increased by adding to the borax half its weight of soda or potassa, and double the quantity of charcoal above-mentioned. According to Berzelius (*Ann. of Phil.*, xxx. 128), boron is most economically obtained by decomposing the borofluoride of potassium. This compound, dry and in powder, is heated in a porcelain crucible with potassium; the reduction goes on quietly, and the fused mass is triturated with water, by which the boron is separated, which is then washed upon a filter with a solution of hydrochlorate of ammonia, and afterwards with alcohol.

Boron is a very deep olive-colored substance, infusible, inodorous, insipid, and a non-conductor of electricity. Its specific gravity exceeds 2. It is not acted upon by air, water (at least after it has been heated to redness), alcohol, ether, or oils. In the state of hydrate it long remains diffused through pure water, and passes through filters; but its precipitation is accelerated by saline solutions. It undergoes no change when heated in close vessels; but when nearly red-hot in the air, it takes fire and burns with difficulty into *boracic acid*. It is more easily oxidized by the action of nitric acid: the pure hydracids have no action upon it, but nitrohydrochloric acid converts it into boracic acid, and nitrohydrofluoric acid into fluoride of boron. At a high temperature it rapidly decomposes nitre, even with explosive violence; under the same circumstances, it also decomposes and deflagrates with the hydrate and car-

bonate of potassa: in the former case water is decomposed, and hydrogen evolved; in the latter, carbonic oxide is evolved in consequence of the decomposition of carbonic acid; in both cases borate of potassa is the result.

BORACIC ACID. BO_3 . This which is the only known compound of boron and oxygen, was first obtained by Homberg, in 1702, and was used in medicine under the name of *sedative salt*. Its composition was demonstrated by Davy in 1807. It is usually obtained by dissolving the salt called *borax* in hot water, and subsequently adding half its weight of sulphuric acid; as the solution cools, white scaly crystals appear, which, when washed with cold water, are nearly tasteless, and which consist of boracic acid combined with about 40 per cent. of water, and retaining a little sulphuric acid, which it loses at a red heat. A hot saturated solution of borax may also be decomposed by hydrochloric acid; the hydrated boracic acid, which falls as the liquid cools, may then be washed and dried: heated in a platinum crucible, it fuses into a hard transparent glass. Its specific gravity before fusion is 1.48; after fusion, about 1.8. At a white heat this acid slowly sublimes when exposed to air. It sometimes happens, that flashes of electric light are observed during the spontaneous cracking of a mass of fused boracic acid.

The *crystallized hydrate of boracic acid* is soluble in about 30 parts of cold, and 3 of boiling water: the latter solution deposits it in pearly scales as it cools: it is also soluble in alcohol, to the flame of which it communicates a beautiful green color. It dissolves in several of the strong acids, especially the sulphuric. It has little taste, and feebly reddens vegetable blues; it renders turmeric brown, like an alkali. (FARADAY, *Quarterly Journal*, xi. 403.) The anhydrous acid becomes opaque when exposed to air; it is very fusible, and forms fusible combinations with many of the metallic oxides; hence, it is often used as a flux. When boracic acid is perfectly pure, and slowly deposited from its aqueous solution, it forms small prismatic crystals.

According to Davy, boron, when burned in oxygen, or acidified by nitric acid, combines with about 68 *per cent.* of oxygen; and with this, the theoretical estimate of Berzelius coincides: there is, however, a difference of opinion as to the atomic constitution of the boracic acid, and the equivalent of boron. L. Gmelin and Berzelius now represent the boracic acid as BO_3 , and Gmelin assumes the equivalent of boron as 10.8. Adopting 11 as the equivalent of boron, anhydrous boracic acid will be constituted by

						Berzelius.	
Boron	1	...	11	...	31.43	...	31.19
Oxygen	3	...	24	...	68.57	...	68.81
<hr/>						<hr/>	
Boracic acid	1		35		100.00		100.00

And the crystallized hydrate will consist of

						Berzelius.		Davy.	
Anhydrous boracic acid	1	...	35	...	56.45	...	56	...	57
Water	3	...	27	...	43.55	...	44	...	43
<hr/>						<hr/>		<hr/>	
Crystallized boracic acid	1		62		100.00		100		100

These crystals, when dried at 212° , lose half their water.

The green tint communicated by boracic acid to the flame of alcohol is so peculiar that it is resorted to as an indication of the presence of the acid. If a salt, for instance, is suspected to contain boracic acid, a little sulphuric acid may be added, and the mixture dried by a gentle heat: this will separate the boracic acid, and if any chlorine or hydrochloric acid be present (which also gives a greenish-blue flame) it will be dissipated. Alcohol is then poured upon the dry mass, and a bit of cotton moistened with the alcoholic solution and inflamed: if the quantity of boracic acid is very minute, the green tint does not at first appear, but, after a time, especially if the cotton be moved about with a glass rod, the point of the flame assumes a green hue: the absence of copper must always be ensured.

Native Boracic Acid occurs among the volcanic products of the Lipari Islands, whence it has been collected for the manufacture of borax; it also exists in the hot springs of that district, and in those of Sasso, in the Florentine territory; hence the term *sassolin* applied to it by some mineralogists. It also occurs in *Datolite*, *Boracite*, and some other minerals, and in native *Borax*. An account of the Tuscan *lagoni*, whence large quantities of this acid are obtained, is given by Dumas (*Chim. app. aux Arts*, i. 379), and by Payen (*Chem. Gaz.*, Feb. 1843).

BORATES. The affinity of boracic acid for bases in the humid way is feeble, little exceeding that of carbonic acid; but at a red heat it displaces all the volatile acids. The borates are mostly fusible into a vitreous mass which acquires various and often very characteristic colors from the different metallic oxides, hence one of the uses of borax in qualitative blow-pipe trials. A red-hot platinum wire dipped into a pulverised mixture of equal parts of a boracic salt and bisulphate of potassa gives the peculiar green tint above mentioned to the flame of the blow-pipe. With the exception of the salts of ammonia, potassa, soda, and lithia, the borates are all of difficult solubility.

BORACIC ACID AND AMMONIA. BORATE OF AMMONIA. According to L. Gmelin, a biborate of ammonia, $\text{NH}_3, 2\text{BO}_3, 5\text{HO}$, is obtained by dissolving boracic acid in slight excess of warm solution of ammonia; the temperature rises, and by slow cooling opaque rhombic octohedra are deposited, which effloresce by exposure to air, and give off ammonia; they are soluble in 12 parts of cold water and the solution, when heated, loses ammonia. This salt consists of

			L. Gmelin.		Soubeiran.		Arfwedson.	
Ammonia.....	1	17	12.88	12.5	13.544	12.88		
Boracic acid ...	2	70	53.03	51.0	50.000	63.34		
Water	5	45	34.09	36.5	36.452	23.78		
<hr/>								
Biborate of ammonia	1	132	100.00	100.0	99.996	100.00		

When this salt is dissolved in a strong warm solution of ammonia, in a closed vessel, it deposits crystals of a *subborate*, $3\text{NH}_3, 4\text{BO}_3, 6\text{HO}$; containing therefore,

					Arfwedson.	
Ammonia.....	3	51	20.81	21.55		
Boracic acid.....	4	140	57.14	55.95		
Water	6	54	22.05	22.50		
<hr/>						
Subborate of ammonia	1	245	100.00	100.00		

QUADRIBORATE OF AMMONIA. $\text{NH}_3, 4\text{BO}_3, 7\text{HO}$. This salt is formed by saturating warm solution of ammonia by boracic acid, and slow evaporation: it yields transparent, irregular, six-sided prisms, at first tasteless, then hot and bitter, and having alkaline reaction on test paper. It dissolves in eight parts of cold water, and gives out ammonia when heated. (L. GMELIN, *Handbuch*. SOUBEIRAN, *Jour. de Pharm.*, xi. 34. ARFWEDSON, *Poggend.*, ii. 130.) This salt contains

				Arfwedson.			L. Gmelin.		
Ammonia	1	...	17	...	7.72	...	7.9	...	5.9
Boracic acid	4	...	140	...	63.63	...	64.0	...	63.4
Water	7	...	63	...	28.65	...	28.1	...	30.7
<hr/>									
Quadriborate of ammonia....	1		220		100.00		100.0		100.0

CHLORIDE OF BORON. BCl_3 . Sir H. Davy first observed the combustion of boron in chlorine, and afterwards Berzelius found that on passing dry chlorine over heated boron, or over a red-hot mixture of dry boracic acid and charcoal, a permanent gas was formed which might be freed from chlorine by passing it through mercury, great care being taken to exclude all moisture. (In this latter case, the gaseous chloride of boron is mixed with carbonic oxide. $\text{BO}_3 + 3\text{C} + 3\text{Cl} = \text{BCl}_3 + 3\text{CO}$.) This gas has a pungent odor; it is colorless, fumes in contact of air, is rapidly absorbed by water, soluble in alcohol, and forms a liquid compound with ammonia. (*Ann. of Phil.*, xxvi. 129.) Its specific gravity, according to Dumas, is 3.942. When absorbed by water, it forms boracic and hydrochloric acid. It consists of

							Dumas.
Boron	1	...	11	...	9.24	...	9.29
Chlorine	3	...	108	...	90.76	...	90.71
<hr/>							
Chloride of boron....	1		119		100.00		100.00

IODIDE and BROMIDE OF BORON are unknown.

FLUORIDE OF BORON. FLUOBORIC ACID. BF_3 . In the hope of obtaining anhydrous fluoric acid, Gay Lussac and Thenard heated a mixture of vitrified boracic acid and fluor-spar to whiteness in a gun-barrel; the result was not as they had anticipated, but a peculiar gaseous compound was obtained, to which they gave the name of *fluoboric acid*, and biborate of lime remained in the tube ($7\text{BO}_3 + 3\text{CaF} = 3[\text{CaO}, 2\text{BO}_3] + \text{BF}_3$). (*Mem. d'Arcueil*, ii. 317.) Dr. John Davy obtained the same gas by heating in a glass retort, over a lamp, a mixture of 1 part of vitrified boracic acid, 2 parts of finely-powdered fluor-spar (fluoride of calcium), and 12 parts of sulphuric acid (*Phil. Trans.*, 1812); but in this case it is generally contaminated by fluosilicic gas, derived from the glass. It must be collected over dry mercury.

Fluoboric gas, according to Dr. Davy, has a specific gravity = 2.371, according to Dumas = 2.31; it is colorless, of a pungent odor, highly deleterious to respiration, and extinguishes flame. It strongly reddens litmus; and when bubbles of it are allowed to escape into the air, they produce a remarkably dense and white fume, in consequence of their eager attraction for, and combination with, aerial moisture. Water takes up 700 times its volume of the gas, increasing in volume and density,

and forming a caustic and fuming solution, in which Berzelius found boracic and hydrofluoric acids in combination, (*borohydrofluoric acid*:) it would seem, therefore, that fluoboric gas decomposes water, and that the hydrogen of the water unites to the fluorine to form hydrofluoric acid, and the oxygen to the boron, to form boracic acid, $\text{BF}_3 + 3\text{HO} = 3\text{HF} + \text{BO}_3$. When the solution is concentrated, the hydrofluoric and boracic acids again decompose each other, and the original compound is reproduced. Neither the gas nor the liquid acid act upon glass, but they speedily decompose almost all organic substances: a piece of paper introduced into the gas standing in a tall jar over mercury, causes its rapid absorption, and becomes charred as if burned, in consequence of the abstraction of the elements of water. When potassium is heated in fluoboric gas, it burns, and a brown compound results, consisting of boron and fluoride of potassium: the latter may be dissolved in water, and pure boron remains. Regarding fluoboric gas as a binary compound, it consists of

					Berzelius.
Boron.....	1	11	16.17
Fluorine.....	3	57	83.83
<hr/>					<hr/>
Fluoboron	1		68		100.00

FLUOBORATES OF AMMONIA. If one measure of fluoboric gas be admitted to one of ammonia, in a jar over mercury, complete condensation ensues, and a white opaque solid results, which sublimes without decomposition when gently heated, and which, in the presence of water, affords hydrofluat and borate of ammonia. When 1 volume of fluoboric gas is mixed with 2 volumes of ammoniacal gas, they condense into a transparent liquid, which, when heated, or exposed to the air, loses half its ammonia, and passes into the solid compound. 1 volume of fluoboric gas and 3 of ammonia also become condensed into a liquid resembling the preceding. (J. DAVY.) The relation of the atomic weight to the volume of fluoboric gas has not been satisfactorily determined, nor have the general characters of these compounds been adequately examined; so that we are unable accurately to determine their atomic constitution: they are generally represented as NH_3, BF_3 ; $2\text{NH}_3, \text{BF}_3$; and $3\text{NH}_3, \text{BF}_3$.

BORON AND NITROGEN. ÆTHOGEN. By heating a mixture of boracic acid and mellone, or of 58 cyanide of mercury, 5 sulphur, and 7 dry boracic acid, a compound is produced, according to Balmain, of nitrogen and boron: it attracts moisture and forms ammonia by exposure to air. It combines with metals, forming compounds remarkable for luminosity before the blowpipe. (*Phil. Mag.*, July, 1842, and *Mem. Chem. Soc.*, i. 149.)

SULPHURET OF BORON. When boron is strongly heated in sulphur vapor, it burns and produces an opaque white compound, which by the contact of water yields boracic acid and sulphuretted hydrogen. (BERZELIUS.)

SUCH are the general properties of the simple non-metallic substances, and of their mutual combinations; they have been described in the order suggested at page 262, and I trust that the principles of nomenclature there adverted to will now be intelligible, and that the arrangement, adopted in respect to them and their compounds, will be found sufficiently perspicuous and convenient to justify the application of a similar method to the *metals*, and to the combinations which they form with the bodies described in this chapter. I have already observed, that, strictly speaking, the basis of Silica, under the name of *silicon*, should have been placed among the non-metallic elements, and that the analogies which it bears to *boron* are such, as to justify its dismissal from the metals: but others of its characters have been but imperfectly examined; and, if general analogies are made the basis of our arrangements, it would not be difficult to show that, in many other cases, the line of demarcation between the non-metallic and metallic bodies is so indistinct, as to render it probable that they may gradually merge into each other, and that the distinctive characters by which it has been attempted to separate them, are not well-founded: these matters will be more evident when the individual metals are examined; thus, the striking analogy that subsists between sulphur and arsenic, tellurium and selenium, is such as, on many points, closely to approximate those substances: and some of the other acidifiable metals are, by a similar analogy, related to arsenic; and, on the other hand, carbon approximates so closely in certain of its characters, to those considered appropriate to the metals, as, in the opinion of some, to justify its being placed among them: and the claims of hydrogen to rank as a gaseous metal, are by no means inconsiderable. In short, the more we examine into the details of our artificial arrangements, the less consistent do we in general find them with nature; so that they should always be regarded as merely tending to the convenience of description and discussion, and not as possessing any weightier claims upon our consideration. Hence, I have not thought it worth adverting, in detail, to the opinions of contemporary writers upon this subject, or enumerating the grounds upon which they have contrived plausibly to arrange the subjects of chemistry in an order extremely at variance with that which is here adopted. To describe those substances first, which, in the common acceptation of the term, are most important, which are of most frequent occurrence, and most influential in the majority of chemical phenomena, and to associate the description of compounds with those of their elements, seems to me to be the system which least perplexes the student, and is, therefore, that upon which the preceding and succeeding portions of this work are founded.

PART II.

CHEMISTRY OF THE METALS.

CHAPTER VI.

OF THE METALS, AND THEIR COMBINATIONS.

THE metals constitute a numerous and important class of simple substances. They are forty-three in number, and are enumerated in the following table, with their equivalent numbers and symbols annexed.

	Equiv.	Symbol.		Equiv.	Symbol.
1. Gold	200	Au	23. Palladium	54	Pd
2. Silver	108	Ag	24. Rhodium	52	R
3. Copper	32	Cu	25. Iridium	99	Ir
4. Iron	28	Fe	26. Osmium	100	Os
5. Mercury	100	Hg	27. Cerium	46	Ce
6. Tin	59	Sn	28. Potassium	40	K
7. Lead	104	Pb	29. Sodium	24	Na
8. Zinc	32	Zn	30. Lithium	7	L
9. Bismuth	213	Bi	31. Barium	69	Ba
10. Antimony	129	Sb	32. Calcium	20	Ca
11. Arsenic	75	As	33. Strontium	44	Sr
12. Cobalt	30	Co	34. Magnesium	12	Mg
13. Platinum	99	Pl	35. Silicium	15	Si
14. Nickel	28	Ni	36. Aluminum	14	Al
15. Manganese	28	Mn	37. Yttrium	32	Y
16. Tungsten	100	W	38. Glucinum	5	G
17. Tellurium	64	Te	39. Zirconium	23	Zr
18. Molybdenum	48	Mo	40. Cadmium	56	Cd
19. Uranium	60	U	41. Thorium	60	Th
20. Titanium	24	Ti	42. Vanadium	68	V
21. Chromium	28	Cr	43. Lanthanum	44	La
22. Columbium	185	Ta			

Of these metals the first seven were known in very remote ages. The ancients designated them by the names of the planets, to which they were supposed to have some mysterious relation; and each was denoted by a particular symbol, representing both the metal and the planet. (In respect to the origin and application of these symbols, see BECKMANN'S *History of Inventions*.)

Gold	was the Sun,	and was thus represented	☉
Silver	„ Moon	„	☾
Mercury	„ Mercury	„	☿
Copper	„ Venus	„	♀
Iron	„ Mars	„	♂
Tin	„ Jupiter	„	♃
Lead	„ Saturn	„	♄

Zinc was not known to the ancients, though they were probably acquainted with its ores, and with their property of forming brass when fused with copper. (PLINY, lib. xxxiv., cap. 2 and 10.) The word *Zinc* first occurs in the writings of Paracelsus, who died in 1541. Bismuth is mentioned in the *Bermannus* of Agricola, written about 1530. Antimony was first obtained in its pure state by Basil Valentine towards the end of the fifteenth century; it is described in his *Currus Triumphalis*

Antimonii. Arsenic and Cobalt were discovered by Brandt in 1733 (*Acta Upsal.*, 1733 and 1742); the ores were known at a much earlier period. Platinum was first recognised as a peculiar body in 1741, by Mr. Charles Wood, Assay-Master in Jamaica. (*Phil. Trans.*, vol. xlv.) In 1751, the distinctive characters of Nickel were shown by Cronstedt (*Stockholm Transactions*), and Manganese was obtained by Gahn in 1774 (BERGMAN'S *Opuscula*, vol. ii.) Tungsten was discovered by MM. Delhuyart, in 1781 (*Mémoires de Toulouse*). Tellurium and Molybdenum by Müller and Hielm, in 1782 (CRELL'S *Annals*, 1790 and 1798). Uranium by Klaproth in 1789. Titanium by Gregor, in 1789 (*Jour. de Phys.*, xxxix.) Chromium by Vauquelin, in 1797 (*Ann. de Ch.*, vol. xxv.) In 1802, Hatchett discovered Columbium. (*Phil. Trans.*) Palladium and Rhodium were discovered by Wollaston; and Iridium and Osmium by Tennant, all in 1803. (*Phil. Trans.*) Cerium was announced in 1804, by Hisinger and Berzelius. (GEHLEN'S *Journal*, ii.) Potassium and Sodium were discovered in 1807, by Davy, whose experiments also led to the discovery of the metallic nature of the ten following bodies. (*Phil. Trans.*) Stromeyer discovered Cadmium in 1818 (*Ann. of Phil.*, xiii.) Thorium was discovered by Berzelius in 1829 (*Poggend. Ann.*, xvi.), Vanadium by Seftström in 1830 (*Ann. Ch. et Ph.*, xlvi.), and Lanthanum by Mosander, in 1838. (*Poggend.*, xlvi. 648.)

Metals are chiefly found in the earth in *veins* which traverse the granitic, schistose, and limestone rocks; they also occur, although comparatively rarely, in rounded and detached fragments and nodules, disseminated through certain alluvial and diluvial strata. They seldom occur in an uncombined state, but almost always united to other substances, as in the following classes:

i. *Native metals* are those which occur pure or alloyed, such as platinum, rhodium, iridium, osmium, gold, silver, mercury, copper, antimony, arsenic, and tellurium.

ii. *Metals combined with simple non-metallic substances.* The compounds belonging to this class are the *native metallic oxides*, and *native chlorides*; *iodides* and *bromides* are extremely rare; and there are few *fluorides*. The *native metallic sulphurets* are a numerous and important series of ores. The *seleniurets* are rare. There are no native carburets, hydrurets, phosphurets, nor borurets.

iii. *Metals in combination with acids; Metallic Salts.* Of these the most common are the native *carbonates*, *sulphates*, and *phosphates*; there are a few native *borates*; and a few species belong also to this class in which the oxide is united to a *metallic acid*: such as the *native arseniates*, *chromates*, *tungstates*, *molybdates*, and *vanadiates*.

PROPERTIES OF THE METALS. *Opacity, Lustre, &c.* The metals, as a class, are characterized by *opacity*, and a peculiar *lustre*. Their *opacity* is such, that even when extended into very thin leaves, they generally transmit no light; silver leaf, only one one-hundred-thousandth of an inch in thickness, is perfectly opaque. Gold, however, when beaten out into leaves one two-hundred-thousandth of an inch in thickness, transmits green rays of light; very thin films of some other metals also transmit certain rays of light, and the alloy of gold and silver transmits under similar circumstances, blue rays. Their *lustre* depends upon their great

power of reflecting light, in consequence of their opacity. They are excellent conductors of heat and of electricity, (see pages 52, 150, and 211,) and are cations, or electropositive bodies; that is, when their compounds are decomposed by the electric current, they are given off at the cathode, or negative electrode. (See p. 221.)

The polished metals are very imperfect radiators and receivers of heat (page 114); but they are excellent reflectors both of light and heat (page 106), and hence their peculiar fitness for the construction of mirrors.

Whenever the polish of the metallic surface is impaired, its power of reflecting heat suffers a proportionate diminution, while its power of absorbing, and also of radiating heat, is proportionably increased. (See page 106.)

Crystallization. Metals are susceptible of assuming the crystalline form. With many this may be effected by fusion and slow cooling, and especially by suffering a ladle, or crucible, filled with the melted metal, to concrete externally, and then perforating the solid crust, and pouring out the liquid interior; the cavity so formed will then be lined with crystals: this mode of proceeding answers extremely well with bismuth, which furnishes a singular congeries of cubic crystals. (p. 8.) When the metals are precipitated by each other, they often crystallize during their deposition, as is seen in the precipitation of silver by mercury, and in that of lead by zinc. A stick of phosphorus immersed in a solution of silver becomes incrustated with beautiful metallic crystals, which, after some time, perfectly encase the phosphorus. Gold is occasionally deposited in a crystalline form, from its ethereal solutions. Some curious facts relating to this subject, will be found in a paper by Professor Daniell, "On certain phenomena resulting from the action of Mercury upon different Metals." (*Royal Inst. Journal*, i. 1.) During the electrolysis of metallic solutions, especially where low powers are employed, beautiful metallic crystals are also occasionally obtained.

Specific Gravity. There is the greatest difference in the *specific gravity* of the different metals, the heaviest and lightest solids being included in the list. Their specific gravity is also in some instances a little increased by hammering, rolling, and some other mechanical processes by which they are permanently compressed. The principal metals, arranged according to their specific gravities, stand as follow. (Temp. 60°, Water = 1.000.) The variations to which their densities are liable are stated under the individual metals.

Platinum	20.98	Uranium.....	9.00	Zinc	7.00
Gold	19.258	Copper	8.89	Manganese ...	6.85
Iridium	18.680	Cadmium	8.60	Antimony.....	6.70
Tungsten]	17.59	Cobalt.....	8.53	Tellurium.....	6.10
Mercury	13.568	Nickel.....	8.27	Arsenic.....	5.8
Palladium	11.80	Iron	7.78	Titanium	5.3
Lead	11.35	Molybdenum ...	7.40	Sodium	0.972
Silver	10.47	Tin	7.30	Potassium	0.865
Bismuth	9.80				

Malleability. Among the metals, some are *malleable*, others *brittle*; hence the ancient division into *perfect* and *semi-metals*. Common gold-leaf is not more than $\frac{1}{200000}$ th of an inch in thickness, and five grains are sufficient to cover a surface of more than 270 square inches. This

capacity of being extended by the hammer, belongs to the following metals:

Gold	Tin	Lead	Nickel	Sodium
Silver	Cadmium	Zinc	Palladium	Frozen Mercury.
Copper	Platinum	Iron	Potassium	

Ductility. The malleable metals are also *ductile*; that is, they admit of being drawn out into wires. Silver, for the purposes of embroidery, is commonly drawn down to wire of 1-500th of an inch in thickness. A grain of gold may be drawn into 500 feet of wire; by enveloping it in silver, Dr. Wollaston found that it might be so extended, as that 550 feet weighed only one grain; its thickness, therefore, not exceeding 1-5000th of an inch. The coating of silver was removed by dilute nitric acid. In the same way he produced platinum wire of a diameter not exceeding 1-30000th of an inch in thickness. (*Phil. Trans.*, 1813, p. 114.) The following metals are arranged according to their ductility:

Gold	Iron	Tin	Palladium
Silver	Copper	Lead	Cadmium.
Platinum	Zinc	Nickel	

Tenacity. Different metallic wires are possessed of different degrees of *tenacity*, by which is meant the power of supporting a weight without breaking. According to the experiments of Guyton Morveau, the following are the weights sustained by wires 0·787 of a line in diameter (*Ann. Ch. et Ph.*, LXXI.):

	lbs. dec. avoir. parts.		lbs. dec. avoir. parts.
A wire of iron supports	549·250	A wire of gold supports	150·753
„ copper.....	302·278	„ zinc.....	109·540
„ platinum.....	274·320	„ tin	34·630
„ silver	187·137	„ lead	27·621

Baudrimont found the tenacity of metals greatly diminished by the process of annealing: thus a wire of soft iron, which sustained a weight of 26lbs., only sustained 12lbs. after having been annealed; and one of copper, which sustained 22lbs. before annealing, was broken by 9lbs. after annealing. (*Ann. Ch. et Ph.*, LX. 78.)

Brittleness. The following metals are brittle, and most of them may even be reduced to powder:

Antimony	Cerium	Columbium	Tellurium	Uranium
Arsenic	Chromium	Manganese	Titanium	Rhodium.
Bismuth	Cobalt	Molybdenum	Tungsten	

Hardness. Few of the metals, when pure, are very *hard*, and many so soft as to yield to the nail. In the following table, some of the metals are arranged in the order of their hardness. (DUMAS.)

Titanium	} Harder than steel.	Chromium	} Scratch glass.
Manganese		Rhodium	
Platinum	} Scratched by calc-spar.	Nickel	} Scratched by glass.
Palladium		Cobalt	
Copper		Iron	
Gold		Antimony	
Silver		Zinc	
Tellurium		Lead	} Scratched by the nail.
Bismuth		Potassium	
Cadmium		Sodium	} Soft as wax (at 60°)
Tin		Mercury	
			Liquid.

Elasticity and sonorousness belong to the hardest metals only, and are most evident in certain alloys. (On the influence of temperature on the elasticity of metals, see WERTHEIM, *Ann. Ch. et Ph.*, Septembre, 1845.)

Odor and Taste. There are several of the metals which have a peculiar odor, especially when they are rubbed, or their temperature otherwise slightly elevated; this is more especially the case with copper, iron, and tin. It has been supposed that these metals owe their smell and taste to some foreign matter, and possibly electricity and moisture may be concerned; yet many of the most oxidable metals are entirely destitute both of taste and odor.

Fusibility. The metals are all susceptible of fusion by heat, but the temperatures at which they liquify are extremely various. Mercury is fluid at common temperatures, and requires to be cooled to -39° before it congeals. Potassium melts at about 136° , and sodium at 190° ; tin at 442° ; lead at 612° ; zinc at 770° ; and antimony at about 850° . Silver, gold, and copper, require a bright cherry red heat; iron, nickel, and cobalt, a white heat; manganese and palladium, an intense white heat; molybdenum, uranium, tungsten, and chromium, are only very imperfectly agglutinated at the highest temperatures of our furnaces; and titanium, cerium, osmium, iridium, rhodium, platinum, and columbium, require the intense heat produced by an inflamed current of oxygen and hydrogen, or that of Voltaic electricity. Arsenic volatilizes before it fuses; but in general, at higher temperatures than that required for their fusion, the metals are volatile, and many of them may be distilled in close vessels. Mercury is volatile at common temperatures, or at least when above 40° , a piece of gold leaf suspended over it becomes slowly whitened; cadmium, arsenic, potassium, sodium, tellurium, and zinc, are volatile at a red heat. Gold and silver are converted into vapor when exposed to the intense heat of the focus of a burning lens; and several of the other metals boil and evaporate under similar circumstances.

In the following table the metals are arranged in the order of fusibility. (TURNER, *Elements of Chem.*)

		Fahrenheit.	
Fusible below a red heat.	Mercury	-39°	Different Chemists.
	Potassium	136°	} Gay Lussac and Thenard.
	Sodium	190°	
	Tin	442°	Crichton.
	Cadmium	450°	Stromeyer.
	Bismuth	497°	} Crichton.
	Lead	612°	
	Tellurium: rather less fusible than lead	...	Klaproth.
	Arsenic, undetermined.		
	Zinc	773°	Daniell.
Infusible below a red heat.	Antimony, little below redness.		
	Silver	1873°	} Daniell.
	Copper	1996°	
	Gold	2016°	
	Cobalt; rather less fusible than iron.		
	Iron, Cast	2786°	Daniell.
	Iron, malleable } require the highest heat Manganese } of a smith's forge. Nickel, nearly the same as cobalt.		

Infusible
below
a red
heat.

}	Palladium
	Molybdenum
	Uranium
	Tungsten
	Chromium
	Titanium
	Cerium
	Osmium
	Iridium
	Rhodium
	Platinum
	Columbium

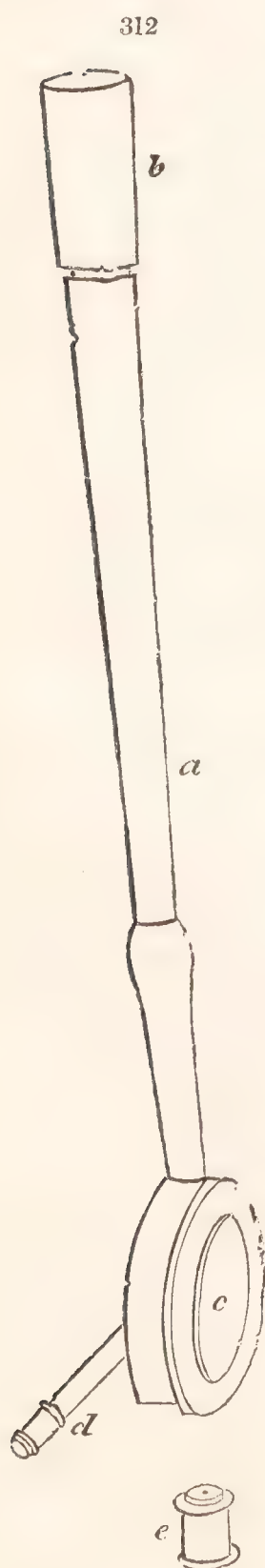
Almost infusible, and not to be procured in buttons by the heat of a smith's forge, but fusible before the oxyhydrogen blowpipe.

USE OF THE BLOWPIPE. In the examination of the effects of heat and air upon metallic and mineral substances, the *blow-pipe* is a most useful and necessary auxiliary to our other operations; it affords a simple

and convenient means of heating to a very high degree, and almost instantaneously, any substance sufficiently small to be enveloped in its flame; and the experienced eye is thus frequently enabled to anticipate, with much precision, the nature of the substance submitted to experiment. There are numerous forms of the blow-pipe, among which, that represented in fig. 312 is perhaps the most convenient. It consists of a brass tube *a*, with an ivory mouth-piece *b*; the other end of the tube terminates in a circular box, from which issues the small tube *d*, moveable in any direction round the centre *c*, by which any degree of obliquity may conveniently be given to the flame; *e* is a brass jet which fits upon the tube *d*.

The following observations respecting the use of the blow-pipe, and its action upon several substances, are extracted from CHILDREN'S *Essay on Chemical Analysis*; a work from which the student may derive much valuable information. (See also PARNELL, *Elements of Ch. Anal.*, p. 93.)

A continued stream of air is absolutely essential, to produce which, without fatigue to the lungs, an equable and uninterrupted inspiration must be maintained by inhaling air through the nostrils, whilst that in the mouth is forced through the tube by the compression of the cheeks. A little practice will make this operation easy, but at first considerable lassitude is generally experienced in the buccinator muscles. (Upon this subject, see FARADAY'S *Manipulation*, s. iv.) After habit has rendered the operation familiar, a current may be kept up for ten or fifteen minutes, without inconvenience. A large wax-candle supplies the best flame, which being urged by the blast, exhibits two distinct figures; the *internal* flame is conical, blue, and well defined, at the apex of which the most violent degree of heat is excited: the *external* is red, vague, and undetermined, and of very inferior temperature to the former.



The substance to be submitted to the action of the blow-pipe, which should not be larger than a small pepper-corn, must be supported either on charcoal, or a slip of platinum or silver foil, or be held in a pair of platinum pincers. In the first case it may be placed in a cavity in the charcoal, and another piece laid over it to prevent its being carried off by the blast. The metallic supports are used when the subject of the experiment is intended to be exposed to the action of heat only, and might be altered by contact with the charcoal. If a very intense heat be required, the foil may be laid on charcoal. Salts and volatile substances are to be heated in glass tubes, closed at one end, and enlarged according to circumstances, so as to form small matrasses.

The exterior flame should first be directed on the substance, and when its action is known, then the interior blue flame. Notice should be taken, whether the matter decrepitates, splits, swells up, liquifies, boils, vegetates, changes color, smokes, is inflamed, becomes obedient to the magnet, &c.: when the action of heat alone has been ascertained, it will be necessary to examine what further change takes place, by fusing it with various fluxes, and also whether it be capable of reduction to the metallic state.

The three most useful fluxes are, the triple phosphate of soda and ammonia, carbonate of soda, and borax. These are to be kept ready pulverized, and when used, a sufficient quantity may be taken up by the moistened point of a knife; the moisture causes the particles to cohere, and prevents their being blown away, when placed on the charcoal. The flux must be melted into a clear bead, and the substance then placed on it, and submitted, first to the action of the exterior, and then to that of the interior flame. The appearances which ensue must be observed; as, 1st. If the substance be dissolved, and whether with or without effervescence. 2nd. The transparency, and color of the glass whilst cooling. 3rd. The same circumstances when cold. 4th. The nature of the glass formed by the exterior flame. 5th. Also by the interior flame. 6th. The particular appearances with each of the fluxes.

Carbonate of soda does not form a bead on charcoal, but with a certain degree of heat is absorbed; it must therefore be added in very small quantities, and a gentle heat used at first, which will promote combination without the absorption of the alkali. Some minerals combine readily with very small portions of soda, but difficultly if more be added, and are absolutely infusible with it in great excess; and when the substance has no affinity for this flux, it is absorbed by the charcoal, and no combination ensues. When the mineral contains sulphur or sulphuric acid, the glass acquires a deep-yellow color, which by the light of a lamp appears red, as if produced by copper. If the glass bead become opaque as it cools, so as to render the color indistinct, it should be broken, and a part of it mixed with more of the flux, till the color becomes purer, and distinct. To make the color more perceptible, the bead may be flattened whilst soft, or drawn out to a thread.

If it be wished to *oxidate* a metallic substance, combined with either of the fluxes, the glass is first heated intensely, and when fused, gradually withdrawn from the point of the blue flame, and the operation repeated as often necessary, using a jet of large aperture. The addition of a little nitre also assists the oxidation. For the *reduction* of metallic oxides, the glass bead is to be kept in fusion on charcoal, as long as it remains on the

surface, and is not absorbed, that the metallic particles may collect into a globule. It is then to be fused with an additional quantity of soda, which will be absorbed by the charcoal, and the spot where the absorption has taken place strongly ignited by a tube with a small aperture. By continuing the ignition, the portion of metal which was not previously reduced will now be brought to the metallic state, and the process may be assisted by placing the bead in a smoky flame, so as to cover it with a soot that is not easily blown off.

The beads which contain metals frequently have a metallic splendor, which is most easily produced by a gentle, fluttering, smoky flame, when the more intense heat has ceased. With a moderate heat the metallic surface remains; and by a little practice it may generally be known whether the substance under examination contains a metal or not. But the glass of borax alone sometimes assumes externally a metallic appearance. When the charcoal is cold, that part impregnated with the fused mass should be taken out with a knife, and ground with distilled water in an agate mortar. The soda will be dissolved; the charcoal will float, and may be poured off: and the metallic particles will remain in the water, and may be examined. In this manner most of the metals may be reduced.

ACTION OF OXYGEN. When the metals are exposed at ordinary temperatures to the action of oxygen, or of common air, which produces analogous, though less powerful effects, they are very differently affected. If the gas be perfectly dry, few of them suffer any change, unless heated in it; they then lose their metallic characters, and form an important series of compounds, the *metallic oxides*, or *calces*, as they were formerly termed, and the term *calcination* is synonymous with *oxidizement* or *oxidation*. A few of the metals resist the action of heat and air so completely, that they may be kept in fusion in an open crucible for many hours without undergoing change. This is the case with platinum and gold; hence they and a few others were called *noble* metals: by passing a strong electric discharge through them, when drawn into very fine wire, they are reduced to the state of impalpable powder, which is sometimes regarded as an oxide; but the appearance ensues in hydrogen as well as in common air, and the oxides of those metals are reducible by heat alone: the appearance, therefore, is probably referable to minute mechanical division only. Other metals readily absorb oxygen when exposed to a temperature approaching a red heat; as iron, mercury, nickel, &c.; others absorb it when in fusion, as lead, tin, antimony, &c.; others at lower, or even at common temperatures, as arsenic, manganese, sodium, potassium, &c. The mutual action, however, of metals and oxygen is apparently much interfered with by their aggregation, for some of them, which under ordinary circumstances are only slowly oxidized by exposure to air and heat, are rapidly acted on when in very fine mechanical division, even at common temperatures; and this would probably be found more generally the case, had we the means of reducing them to extremely fine powder.

Silver, and perhaps one or two other metals, have a peculiar power of absorbing and retaining oxygen at high temperatures and when in fusion, without combining with it, and it escapes when the fused metal solidifies. (See SILVER.)

The different attractive powers of the metals in regard to oxygen is shown by the circumstance of one metal being oxidized at the expense of another: thus the oxide of mercury, heated with metallic iron, produces metallic mercury and oxide of iron; potassium, heated with oxide of manganese, becomes oxidized, and metallic manganese is obtained. Upon the same principle, solutions of metallic oxides in the acids may often be reduced to the metallic state by the immersion of other metals: mercury thus decomposes nitrate of silver; copper decomposes nitrate of mercury; and iron decomposes nitrate of copper. In these cases of metallic precipitation, electricity becomes active the moment that the deposition commences; the precipitating or reducing metal being positive, and that which is precipitated, or reduced, negative. Very beautiful crystalline deposits may thus often be obtained, as where silver is precipitated by mercury, and lead by zinc. Metals which are in this way difficultly thrown down from their solutions in acids, are sometimes easily obtained from their solutions in alkalis, as for instance tungsten and tin.

Many of the metallic oxides are reduced, when in solution, by the protosalts of iron and tin, which by abstracting oxygen pass into the state of persalts, and throw down the reduced metal in a pulverulent form. The protosalts of iron are in these cases preferable to those of tin, inasmuch as the resulting peroxide of iron is generally retained in solution, and the precipitated metal is pure; but the peroxide of tin often falls along with the reduced metal, in consequence of its difficult solubility in most of the acids. Other compounds having high affinities for oxygen, are also occasionally resorted to as deoxidizing agents, such as sulphurous, phosphorous, and formic acids, and several of their salts; and also certain organic substances.

Some of the oxides are decomposed by mere exposure to heat, as those of platinum, gold, silver, and mercury: others require the joint action of heat and some substance having a high attraction for oxygen, such as charcoal. Thus when oxide of lead is heated with charcoal, carbonic acid gas is evolved, and metallic lead obtained. This important process is termed *reduction*, and is performed in various ways, as will appear by reference to the history of individual metals. The reduction of an oxide is also frequently effected by passing a current of dry hydrogen over it in a heated tube; in this case the oxygen is carried off in the form of water. Sometimes the reduction of an oxide is effected by the aid of another metal possessed of a very superior attraction for oxygen, as in the cases cited in the preceding paragraph: and in some cases complicated attractions are directed to the process of reduction, as in the production of potassium by the action of red-hot iron upon hydrate of potassa.

Electricity is an all-powerful agent in metallic reduction, and capable, under certain circumstances, of overcoming the most energetic attractions. This important subject has been discussed and illustrated in a former chapter (p. 219).

Some of the metallic combinations, especially those of gold, are reducible by the agency of *light* (p. 100); the salts of silver are also discolored or partially reduced by the same agency.

The oxidizement of a metal is an essential preliminary to the forma-

tion of its oxy-salts, or, in other words, to its combinations with oxy-acids; and in this respect common chemical nomenclature is inaccurate. Thus we speak of sulphate of *copper*, nitrate of *zinc*, &c., meaning sulphate of *oxide* of copper, nitrate of *oxide* of zinc, &c. This ambiguity is prevented with respect to the alkalis and alkaline earths, the oxides of their bases being characterized by a distinct termination: thus phosphate of *soda* means phosphate of *oxide of sodium*, &c.; a circumstance which induced Sir H. Davy to propose an analogous termination for all the oxides, appropriately applied to their common Latin names: as *Cupra*, for oxide of copper; *Argenta*, for oxide of silver, &c.

Each metal has a certain definite quantity of oxygen with which it combines; and where the same metal unites in more than one proportion with oxygen, in the second, third, and other compounds, it is a multiple of that in the first, consistent with the law of definite proportionals. Thus, 100 parts of mercury combine with 4 of oxygen to produce the black oxide, and with 8 to produce the red oxide. Copper also forms two oxides; in the one 12.5 of oxygen are united to 100 of metal, and in the other 25. Where two oxides only are thus formed, that with the minimum of oxygen is termed the *protoxide*, and that with the maximum of oxygen the *peroxide*; or, in some cases, the term *dioxide* or *suboxide* is substituted for that of protoxide, as indicating a compound of 2 atoms or equivalent proportionals of metal with one of oxygen. Where there are three or four distinct steps of oxidizement, the terms *deutoxide* or *binoxide*, and *tritoxide* or *teroxide*, may be applied to the second and third stages; and where the proportion of oxygen, in three oxides, is in the relation of 1, $1\frac{1}{2}$, and 2, the second is termed a *sesquioxide*. The metallic oxides are generally regarded as *basic* compounds, and form salts with the acids; but in a few cases the combinations of a metal with oxygen are *acid*, and are then distinguished by the usual terminations; thus, *arsenious* and *arsenic acid* imply the two (acid) oxides of arsenic; in other cases the protoxide may be basic, and the peroxide acid, as is the case with chromium, antimony, and some other metals; and in the case of the combination of two metallic oxides, one may generally be regarded as acting the part of a base, and the other that of an acid. Definite combinations of the metallic oxides are common in the mineral kingdom.

Among the combinations of metals with oxygen, some are insoluble in water, or nearly so, and have neither taste nor smell; others are soluble and sour, constituting the *metallic acids*; others are soluble and alkaline, forming the *fixed alkalis* and *alkaline earths*. They are of all colors, and frequently the same metal united to different proportions of oxygen produces compounds differing in color: thus we have the *black* and *red* oxide of mercury, the *green* and the *black* oxide of manganese, &c.

The different oxides of the same metal sometimes form distinct salts with the acids, and in such cases the quantity of acid required to neutralize the oxide bears a direct proportion to the oxygen which it contains. This law was first developed by Gay Lussac (*Mémoires d'Arcueil*, ii. 159), and it will be found to be illustrated in the cases of the oxides of iron, of mercury, tin, and some other metals. It sometimes happens that the same oxide unites with an acid in two proportions, forming two distinct salts, in which case the acid in the second is a multiple of that in

the first. Thus, 48 parts of potassa unite to 22 and to 44 of carbonic acid, forming a *carbonate* and a *bicarbonate* of potassa: so also we have a *sulphate* and a *bisulphate* of potassa; and there are no less than three compounds of oxalic acid with the same base, forming an *oxalate*, a *binoxalate*, and a *quadroxalate* of potassa.

Montizon has attempted to show (*Ann. Ch. et Ph.*, vii. 7) that a relation subsists between the quantity of oxygen with which the metals combine, and their specific gravities; the oxygen being a multiple or sub-multiple of the density; and he has given a table comparing the results deduced from such a theory, with those obtained by analysis.

In reference to an hypothesis originally propounded by Davy (*Elem. of Chem.*), respecting the possible existence of hydrogen in the metals, and of water in their oxides, Gay Lussac has observed that the lightest metals are those which absorb most oxygen in becoming oxides; and that the heavier or denser metals, on the contrary, absorb less oxygen; in other words, the denser metals are those which have the higher equivalents, the lighter metals being represented by lower numbers: this law, though not rigorously exact, is sufficiently so to deserve attention, and if, selecting certain metals, they be divided into two groups, it will be found that where the specific gravity varies from 10 to 20, the atomic weight is about or above 100, but that where the specific gravity is between 8 and 1, or below 1, the atomic weight is about 30.

I.			II.		
Metal.	Sp. Gr.	Atomic Weight.	Metal.	Sp. Gr.	Atomic Weight.
Platinum	20·98	99	Cobalt	8·53	30
Gold	19·20	200	Copper	8·89	32
Iridium	18·60	99	Nickel	8·27	28
Tungsten	17·50	100	Iron	7·78	28
Mercury	13·56	100	Zinc	7·00	32
Lead	11·35	104	Manganese	6·85	28
Silver	10·47	108	Sodium	0·97	24

ACTION OF CHLORINE. All the metals combine with chlorine, and produce a class of compounds termed *metallic chlorides*. There are a few of the metals which resist the action of chlorine at common temperatures, but when heated they all combine with it; some slowly; others rapidly, and with intense ignition. Copper-leaf, powdered antimony, arsenic, &c., burn when thrown into the gas; mercury and iron inflame when gently heated in it; silver, gold, and platinum, quietly absorb it. In these cases, minute mechanical division remarkably accelerates the action. The attraction of chlorine for metals is greater than that of oxygen; consequently when a metallic oxide is heated in chlorine, oxygen is evolved, and a chloride formed; or, in some cases, the oxide is mixed with charcoal and dry chlorine passed over the heated mixture, in which case carbonic oxide is evolved during the formation of the chloride. The insoluble chlorides are also formed by adding solution of chlorine, or hydrochloric acid, or of the soluble chlorides, to the soluble metallic salts. Thus chloride of silver, which is insoluble, is thrown down from the soluble nitrate of silver by solution of chlorine, of hydrochloric acid, and of common salt: hence, too, all the soluble chlorides are recognized, by yielding a white precipitate with solution of nitrate of silver, which is

soluble in ammonia, insoluble in nitric acid, and which, when pure, rapidly blackens by exposure to the sun's rays.

The physical and chemical properties of the chlorides are extremely various. They are nearly of all colors. They are generally unchanged by heat; but some undergo decomposition. Some are soluble, others insoluble, in water. Some permanent in the air, others deliquescent. Several of them decompose water, and form hydrochloric acid, and an oxide. The question respecting the action of water upon the chlorides has given rise to several hypotheses founded on their mutual decomposition, some of which will be adverted to under specific heads. (See DUMAS, in reference to this question. *Ann. Ch. et Ph.*, xliv. p. 263; also H. ROSE, *Chem. Gaz.*, Jan. 1843.) Many of them absorb ammonia, and some in considerable quantity. They are fusible, and most of them crystallizable. Some are extremely volatile at common temperatures, and others fixed at high heats. A few exist, at all ordinary temperatures, in the liquid state. Many of them are decomposed at a red heat by hydrogen, which produces hydrochloric acid, and reduces the metal. Anhydrous sulphuric acid appears not to act upon them; but the common hydrated acid decomposes them, with few exceptions, evolving hydrochloric acid: the theory of these changes is elsewhere explained. (See *Chloride of Sodium*.) Some of the metals rapidly decompose certain chlorides in consequence of their superior attraction for chlorine; thus chloride of silver is decomposed by zinc, chloride of magnesium by potassium, &c.

The same metal often forms more than one compound with chlorine, and these compounds are designated as the oxides. Thus we have *protochlorides*, *bichlorides*, *sesquichlorides*, and *perchlorides*.

Many of the metals decompose gaseous hydrochloric acid, in which case hydrogen is evolved, and a metallic chloride produced; and when metallic oxides are heated in hydrochloric gas, they generally give rise to the formation of a chloride and water.

There are a few metallic oxides which at low temperatures, absorb and retain chlorine, but they hold it by a feeble attraction. The chlorides of potassa and of lime will be described under those bodies. It has also been combined with the oxides of iron, zinc, and copper. (GROUVELLE, *Ann. Ch. et Ph.*, xvii.) These compounds are decomposed by heat and by the acids.

ACTION OF CHLORIC ACID. The compounds of the metallic oxides with chloric acid, or *chlorates*, are decomposed by heat with the copious evolution of oxygen, and a chloride generally remains: they deflagrate when triturated with charcoal or other combustibles. In the neutral chlorates the proportion of oxygen in the base to that in the acid is as 1 to 5, so that in ultimate constitution they resemble the nitrates: their formula being $MO + ClO_5$ or $M + ClO_6$. The *oxychlorates*, or *perchlorates*, have been but little examined. Like the chlorates, they yield oxygen when heated: and the proportion of oxygen in the base to that in the acid is as 1 : 7, their formula being $MO + ClO_7$ or $M + ClO_8$.

ACTION OF IODINE. Iodine combines with all the metals, producing *metallic iodides*, many of which may be directly formed by triturating the metals with iodine, or by gently heating them together. They are all

solid and volatile, generally inodorous, and of variable colors: a few of them are decomposed by heat. Some are soluble in water without decomposition; others decompose water; others are insoluble. The insoluble iodides may generally be formed by adding a solution of iodine or of hydriodic acid, or of an iodide, to the soluble metallic salts. Iodine often combines in more than one proportion with metals, forming *protiodides*, *sesquiodides*, *biniodides*, &c. The iodides are decomposed by chlorine and bromine, and the greater number by oxygen. According to Gay Lussac, when the vapor of iodine is passed over hot lime, baryta, and strontia, it does not expel their oxygen, but unites with them as oxides. These compounds are not very permanent, and are decomposed at a temperature a little exceeding that required to form them. The iodides are decomposed by nitric and sulphuric acids, but not by aqueous hydrochloric acid. By gaseous hydrochloric acid, at a dull red heat, they are converted into chlorides, and hydriodic acid is formed. The (alkaline) soluble iodides dissolve iodine in quantities directly as their state of concentration: these compounds (*ioduretted iodides*) are not definite, and when treated with ether, the iodine is abstracted, and a colorless solution of the iodide remains. (LABOURÉ, *Chem. Gaz.*, Jan. 1844.)

ACTION OF IODIC ACID. The compounds of this acid with the metallic oxides have been but little examined: they are decomposed and converted into iodides by heat, sometimes with the evolution of oxygen only; at others, iodine is also given off. (See RAMMELSBERG, *Poggend. Journ.*, XLIV. 545.) The formula of the iodates resembles that of the chlorates and nitrates, being $MO + IO_5$ or $M + IO_6$. (See also p. 290.)

ACTION OF BROMINE. Bromine combines with the metals and produces *bromides*, analogous in their general habitudes to the chlorides and iodides; they are formed either by the direct action of bromine on the metal, or by that of hydrobromic acid upon the metallic oxide; or, when insoluble, they are precipitated by the addition of the soluble bromides to metallic solutions. Bromine also unites to some of the metallic oxides, and produces bleaching compounds. Chlorine disengages bromine from its binary metallic compounds, and bromine expels iodine from the iodides; so that the attraction of bromine for the metals is intermediate between chlorine and iodine.

The *bromates* are little known. When heated to redness they become *bromides*, by the loss of oxygen. (See a Memoir on the Bromates by M. BERTHEMOT, *Ann. Ch. et Ph.*, XLIV. 382.) The formula of the bromates corresponds with that of the nitrates, chlorates, and iodates, being $MO + BrO_5$. (See p. 294.)

ACTION OF FLUORINE. As fluorine has not been obtained in a separate state, its immediate action upon the metals is not known; but it would probably be energetic. Such of the *fluorides* as are insoluble may be obtained by the medium of a solution of fluoride of potassium, or by precipitation by hydrofluoric acid: the soluble fluorides are formed by digesting the oxides or carbonates in aqueous hydrofluoric acid. The fluorides are not decomposed by oxygen, chlorine, iodine, or bromine; but they are immediately recognised by the evolution of hydrofluoric acid, when

moistened and heated with sulphuric acid, and by their action upon glass under such circumstances.

ACTION OF HYDROGEN. Hydrogen forms permanent compounds with two of the metals only, namely, arsenic and tellurium. It appears to combine with each in two proportions, forming two solid compounds, the *hydrurets* or *hydrogurets* of arsenic and tellurium; and two gaseous compounds, *arseniuretted* and *telluretted hydrogen*. At high temperatures it dissolves potassium, forming *potassiuretted hydrogen gas*. Hydrogen also appears to combine with zinc and antimony, at least it frequently retains a little of those metals in its gaseous state.

There are many of the metallic oxides and chlorides which, at due temperatures, are decomposed by hydrogen: the oxides are reduced with the formation of water, and the chlorides with the production of hydrochloric acid.

ACTION OF WATER. Those metals which are speedily acted upon by common air and oxygen, are also generally capable of decomposing water; some of them rapidly, others slowly. There are some metals which are not acted upon by air deprived of moisture, nor by water deprived of air; but moist air, or water containing air, effects their oxidizement: this appears to be the case with iron, (Dr. MARSHALL HALL, *Quarterly Journ.*, vii. 55,) and also with lead. The metals are frequently classified according to the different degrees of facility with which they decompose water. (KANE, &c.) Water combines with many of the metallic oxides, and produces *hydrated oxides*, or *metallic hydrates*. In these the relative proportion of water is definite. Some are easily decomposed by very moderate heat, as hydrate of oxide of copper; others retain water even when heated to redness, as hydrate of potassa; others are decomposed at a red heat, as hydrate of lime. Salts part with the water contained in them with different degrees of facility, retaining frequently one or more equivalents at a temperature at which other proportionals go off; hence the distinction between *basic water* and water of crystallisation. (See. p. 6.)

ACTION OF NITRIC ACID. The greater number of metals are capable of decomposing nitric acid by the abstraction of a part of its oxygen, and thus of resolving it into some of the other nitric compounds; nitric acid is a very generally acting solvent, therefore, of these bodies. The decomposition of nitric acid by the metals is also not unfrequently accompanied by the formation of ammonia. It dissolves nearly all the metallic oxides, and produces a numerous class of *nitrates*, which, if prepared with heat and with excess of acid, generally contain the metal at its maximum of oxidizement. The nitrates are all decomposed by a red-heat; they give off oxygen and nitrogen, either separate or combined, and the metallic oxide ultimately remains. They are also decomposed when heated with sulphur, phosphorus, or charcoal; and sulphurous, phosphoric, and carbonic acids are formed: the phosphoric, being a fixed acid, remains united to the metallic oxide; while the sulphurous and carbonic acids are usually expelled. The nitrates are decomposed by hydrated sulphuric acid, nitric acid is evolved, and *sulphates* are formed. In the neutral nitrates the proportion of oxygen in the acid is to that in the base

as 5 to 1, so that they are represented by the formula $MO + NO_5$, or M,NO_6 . Thus in the nitrate of potassa, 48 parts of potassa, containing 8 of oxygen, are combined with 54 of nitric acid, containing 40 (8×5) of oxygen; and in the nitrate of oxide of copper, 40 parts of oxide of copper, containing 8 of oxygen, are combined with 54 of nitric acid, containing 40 of oxygen. (See page 343.)

Some of the nitrates are recognised by dropping sulphuric acid into their solutions, and then gradually adding a solution of protosulphate of iron, when a dark-brown or blackish color is produced at the line of contact of the two liquids.

ACTION OF AMMONIA. At high temperatures some of the metals are capable of decomposing ammonia. (p. 353.) Liquid ammonia dissolves several of the metallic oxides, and with some of them forms crystallizable compounds. It dissolves the oxides of silver, copper, zinc, arsenic, antimony, and tellurium; the protoxides of iron, cobalt, and nickel; and the peroxides of tin, mercury, gold, and platinum. These compounds are all decomposed by heat. The compounds of ammonia with the oxides of gold, silver, and platinum, detonate when heated, and the oxide and the ammonia are both decomposed. The combinations of ammonia, with several anhydrous salts, have been examined by H. Rose. (*Ann. Ch. et Ph.*, Lxii. 308.)

ACTION OF SULPHUR. All the metals appear capable of combining with sulphur and forming *sulphurets* or *sulphides*. These are obtained, 1st, By heating the metal in a close vessel, with sulphur; and it not unfrequently happens that, during the combination, the metal becomes intensely ignited, burning as it were in the vapor of the sulphur, and furnishing a striking instance of combustion without the presence of oxygen; this is the case with potassium and sodium, and with the filings or shavings of copper, bismuth, lead, and iron. 2ndly, By heating a mixture of sulphur and a metallic oxide, in which case sulphurous acid escapes, and the metallic sulphuret remains behind. 3rdly, By decomposing the *sulphates*, either by subjecting them to the action of a current of hydrogen gas in a heated tube, or by heating a mixture of the sulphate with charcoal. 4thly, By the action of sulphuretted hydrogen. 5thly, By fusing the metallic oxide with a mixture of carbonate of potassa and sulphur, in which case an alkaline sulphuret is first formed, and sustains a red heat, but at that temperature a portion of its sulphur is imparted to the reduced metal of the oxide. The sulphurets are in general brittle; some have a metallic lustre, and are opaque; others are without lustre, and more or less transparent. Some are fusible, and some volatile. Some are soluble, but the greater number insoluble in water. Where the same metal forms two sulphurets, the sulphur in those containing the largest proportion is a simple multiple of the sulphur in those containing the smallest proportion; hence we have metallic *sulphurets*, *bisulphurets*, and *sesquisulphurets*; and, generally speaking, the sulphurets correspond in number and atomic composition with the oxides. Exposed to the joint agency of air and moisture, some of the sulphurets pass into sulphates. When heated in close vessels, some undergo no change, as those of sodium and potassium; others sublime unaltered, as sulphuret of mercury and sulphuret of arsenic:

others lose a portion of their sulphur, and, if air be admitted, sulphurous acid escapes, and the metal passes into the state of oxide, as sulphuret of lead and sulphuret of copper; and it is thus that these sulphurets are oxidized by the process called *roasting*, previous to their reduction upon the large scale; others again are entirely decomposed, the metal being completely reduced; this happens on heating sulphuret of platinum or of gold. The sulphurets of antimony, bismuth, and silver are decomposed by exposure to hydrogen at a red-heat, but the greater number of the sulphurets are not thus decomposable. (Rose, *Pogg. Ann.*, iv. 109.) Definite compounds of sulphur with some of the metallic oxides, have been obtained by Arfwedson. (*Ann. Ch. et Ph.*, vi. 204.)

There are certain double sulphurets, which Berzelius has designated *sulphur salts*; in these cases he terms the electronegative sulphurets, *sulphur acids*; and the electropositive sulphurets, *sulphur bases*; among the *sulphur acids*, he enumerates the sulphurets of arsenic, antimony, gold, molybdenum, tellurium, tin, and tungsten; he also calls sulphuretted hydrogen, sulphocyanogen, sulphuret of selenium, and sulphuret of carbon, sulphur acids. The principal sulphur bases are the protosulphurets of the metals of the alkalis and alkaline earths, and the hydrosulphuret of ammonia (sulphuret of ammonium).

In analysing sulphurets the sulphur is usually weighed in the state of sulphuric acid combined with baryta; for this purpose the pulverised sulphuret is digested in nitric, or nitrohydrochloric acid, and thus converted either into a soluble or insoluble sulphate. In the former case the filtered solution is decomposed by chloride of barium, and the precipitated sulphate of baryta collected, dried, and weighed, with proper precautions. Sometimes the sulphates are conveniently decomposed by heating them in an atmosphere of chlorine, by which chlorides of sulphur and metallic chlorides are formed. The sulphurets may also be decomposed by passing pure oxygen gas over them, heated to redness: the sulphurous acid formed is conveyed into a solution of chlorine or chloride of soda, by which it is converted into sulphuric acid, and the sulphur weighed as sulphate of baryta: the metal is of course oxidized.

HYPOSULPHUROUS ACID combines with the metallic oxides, and produces a class of salts termed *hyposulphites*. Several of these have been examined by Herschel. (*Edin. Phil. Journal*, i.) In some of their characters they resemble the sulphites: they are easily soluble; of a bitter or sweet taste; and decomposed by a heat below redness, and by almost all other acids. Their solutions readily dissolve chloride of silver. (See p. 402.)

SULPHUROUS ACID combines with many of the metallic oxides, producing *sulphites*; in some instances oxygen is transferred from the oxide to the acid, and sulphates result. Acting upon the metals, sulphurous acid often gives rise to hyposulphites, and sometimes to sulphurets and sulphites. (*Ann. Ch. et Ph.*, July, 1843.)

The *sulphites* are soluble in water, and have a sulphurous taste and smell. Exposed to moist air, they absorb oxygen, and pass into the state of sulphates. They are decomposed by sulphuric acid, which expels sulphurous acid, and the salts are converted into sulphates. When perfectly pure they are not affected by solution of baryta. (See p. 386.)

In analysing the sulphites their acid is usually weighed as sulphuric acid, by previously converting them into sulphates by the action of nitric acid or of chlorine, or of nitrohydrochloric acid; the sulphuric acid is then precipitated by baryta.

HYPOSULPHURIC ACID forms with the metallic oxides a class of *hyposulphates*. They do not afford precipitates with solution of baryta. When heated they evolve sulphurous acid, and are converted into neutral sulphates: when their solutions are boiled with sulphuric acid, sulphurous acid is evolved, but no sulphur is precipitated. (See p. 402.)

SULPHURIC ACID, in its concentrated state, and unaided by heat, is acted upon by a few of the metals only; when diluted, some of them are oxidized at the expense of the water, hydrogen is evolved, and the metallic oxide combines with the acid, producing a *sulphate*. In these cases the hydrogen evolved is the indicator of the quantity of oxygen transferred to the metal; every volume of hydrogen is the equivalent of half a volume of oxygen, and accordingly the production of 100 cubic inches of hydrogen indicates the transfer of 50 of oxygen, or by weight, of about 17.2 grains. As different metals unite to different weights of oxygen, they will obviously evolve different quantities of hydrogen. Thus, if one metal, to become soluble in sulphuric acid, require to be united with 10, and another with 20 *per cent.* of oxygen, the latter will evolve twice the volume of hydrogen, compared with the former. As the evolution of hydrogen, during the solution of a metal in dilute sulphuric acid, is referable to its oxidizement, no hydrogen will be evolved by the action of the acid upon an oxide, but it will be merely dissolved.

The sulphates are an important class of salts. The greater number of them are soluble in water, and the solutions yield a precipitate with the soluble salts of baryta which is insoluble in acids and alkalis. The insoluble sulphates may be recognised by igniting them in fine powder with thrice their weight of carbonate of soda, by which a soluble sulphate of soda is formed: it may be separated by water and filtration, crystallized, and tested by nitrate of baryta. The sulphates of potassa, soda, lithia, lime, baryta, and strontia, resist a white heat without decomposition: the other sulphates evolve, when intensely heated, sulphuric acid, sulphurous acid, and oxygen. Many of them are decomposed at high temperatures by the action of hydrogen, which carries off the oxygen of the acid, and of the base, and leaves a metallic sulphuret. In some cases the sulphur also combines with the hydrogen, and the sulphate thus affords a reduced metal. They are all decomposed at a red heat by charcoal, and most of them are thus converted into sulphurets; carbonic acid, and carbonic oxide, being at the same time evolved. Many of the anhydrous sulphates absorb ammonia, forming definite compounds which are decomposed by heat. (H. ROSE, *Ann. Ch. et Ph.*, LXXII. 309.) In the neutral sulphates, the proportion of oxygen in the acid is to that in the base as 3 to 1. They are therefore represented by the formula $MO + SO_3$. Thus sulphate of soda is composed of 32 soda, containing 8 of oxygen, combined with 40 of sulphuric acid, containing 24 (8×3) of oxygen; and in the sulphate of copper, 40 parts of oxide of copper, containing 8 of oxygen, are combined with 40 of sulphuric acid, containing 24 (8×3) of oxygen.

The sulphates may also be represented by the electrolytic formula $M + SO_4$. (See also p. 398.)

In the analysis of *sulphates*, the acid is weighed in the state of sulphate of baryta; the soluble sulphates are decomposed by the addition of a solution of chloride or nitrate of barium, the liquor having been previously acidified by a little nitric or hydrochloric acid. If the sulphate is insoluble in water, but soluble in dilute acids, pure nitric or hydrochloric acid is used as the solvent. The insoluble sulphates may be decomposed, as above stated, by fusion with dried carbonate of soda, by which sulphate of soda and carbonates of the bases are formed.

There are two well-defined groups of *double sulphates*. In the one there are 2 equivalents of acid and 2 of base, and in the other 2 of base and 4 of acid. Sulphate of potassa and magnesia represents the first group, the formula of which is $KO,SO_3 + MgO,SO_3 + 6HO$; and common alum may be taken as the type of the second group, its formula being $KO,SO_3 + Al_2O_3,3SO_3 + 24HO$. In the first group, sulphate of ammonia may be substituted for sulphate of potassa, and the sulphates of manganese, iron, zinc, copper, cobalt, and nickel, for the sulphate of magnesia. In the second group ammonia or soda may replace the potassa, and the alumina may be replaced by the sesquioxides of manganese, iron, or chromium. All the salts which constitute the alum group contain the same number of equivalents of water, and they all crystallize in the octohedral form.

ACTION OF SULPHURETTED HYDROGEN. When sulphuretted hydrogen combines with metallic sulphurets, it forms one class of the *sulphur-salts*. It seems doubtful whether any of the metals combine with sulphuretted hydrogen. Its combinations with their oxides have been termed *hydrosulphates*, or *hydrosulphuretted oxides*, but it generally happens that in the mutual action of the sulphuretted hydrogen and the oxide, both are decomposed, the hydrogen combining with the oxygen of the oxide to form water, and the sulphur uniting to the metal to form a metallic sulphuret. $MO + HS = MS + HO$. In a few cases the metallic oxide is reduced. Occasionally a compound of metallic sulphuret and a salt of the oxide is thrown down; thus when sulphuretted hydrogen is passed through a solution of pernitrate of mercury, the latter being in excess, the precipitate is a definite compound of pernitrate and sulphuret of mercury. (H. ROSE, *Ann. Ch. et Ph.*, LXvi. 366.) The following table shows the effect of sulphuretted hydrogen and of sulphuretted hydrosulphuret of ammonia upon solutions of several of the metals, as far as *color* of the precipitate is concerned, these precipitates being often resorted to as qualitative tests; but it must be recollected that the formation of the precipitate and its color and characters are often materially affected by the presence of very minute proportions of acids: in analytical operations, therefore, we are often enabled to separate certain metals from each other by adding the precipitant first to an acid solution, and afterwards to the neutralized liquor. The metals, the sulphurets of which are insoluble in acids, are, of course, those which fall in the first instance. The sulphuretted hydrogen may either be used in the form of a saturated aqueous solution, or sulphuretted hydrogen gas may be passed through the metallic solution: the latter method effects the most complete separation of the metal.

METAL.	SOLUTION.	SULPHURETTED HYDROGEN.	HYDROSULPHURET OF AMMONIA.
MANGANESE	Neutral protochloride	No precipitate	Copious ochre-yellow
IRON	Neutral protosulphate	Blackish and small in quantity	Black and abundant
Ditto	Perchloride	Abundant black	Black
ZINC	Chloride	A little opalescent and then milky	Straw-colour and copious
TIN	Acid protochloride	Brown	Deep orange
Ditto	Acid perchloride	At first 0, then yellow and copious	Apple-green
CADMIUM	Chloride	Yellow	Yellow
COPPER	Protochloride	Deep brown	Brown
Ditto	Nitrate	Black	Brown and black
LEAD	Chloride and nitrate	Ditto	Ditto
ANTIMONY....	Tartrate of antimony and potassa	Deep orange red	Bright orange
BISMUTH	Tartrate of bismuth and potassa	Deep brown	Deep brown
COBALT	Chloride	0 but blackish	Copious black
URANIUM	Sulphate	Brown	Blackish brown
TITANIUM	Acid chloride	0	Black
Ditto	Neutral sulphate	0	Green
CERIUM	Protosalts	0	White
TELLURIUM	Sulphate	Black	Black
ARSENIC.....	White oxide	Yellow	Yellow
Ditto	Arsenic acid	Ditto	Ditto
NICKEL	Sulphate	Brown	Black
MERCURY	Acid nitrate	Black, then gray, and black by excess of test	Black by excess of test
Ditto	Acid perntrate	Ditto	Ditto
Ditto	Corrosive sublimate	Brown by excess of test	Ditto
OSMIUM	Solution of oxide	Metallic	Metallic
PALLADIUM	Chloride	Brown	Brown
SILVER	Nitrate	Black and metallic	Ditto
GOLD	Chloride	Black & reduced gold	Yellow
PLATINUM	Ditto	Deep brown	Pale brown

ACTION OF SELENIUM. Selenium acts upon the metals with nearly the same phenomena as sulphur, and in their general characters the *seleniurets* and sulphurets are analogous: when heated in the open fire the selenium burns slowly off with an azure flame, and the odor of radish. The atomic composition of the seleniurets follows that of the sulphurets, and they are best obtained by precipitating the metallic solutions with seleniuretted hydrogen, and then, if biseleniurets are required, the precipitate may be fused with selenium, and the excess driven off by distillation. The *selenites* and *seleniates* are decomposed by sulphurous acid, which throws down the selenium of a red color in the cold, and nearly black at a boiling-heat. Distilled with hydrochlorate of ammonia, selenium passes over. In the selenites the oxygen in the acid is to that in the base as 2 to 1, and in the seleniates as 3 to 1; these salts, therefore, are isomorphous with the sulphites and sulphates.

ACTION OF PHOSPHORUS. Phosphorus combines with the greater number of the metals, forming a series of *metallic phosphurets*. There are three methods of forming them; 1st, by heating a mixture of phosphorus and the metal, or projecting phosphorus upon the metal previously

heated to redness; 2nd, by heating a mixture of the metal or its oxide, with phosphoric acid and charcoal: 3rd, by passing phosphuretted hydrogen over the heated metallic oxide. A very few only of the phosphurets can be obtained in the humid way, for when phosphuretted hydrogen is passed through metallic solutions the metal is either reduced, as in the case of the salts of gold and silver; or peculiar compounds ensue, composed of the metallic salt and the phosphuret, as when the salts of peroxide of mercury are decomposed by phosphuretted hydrogen; or no change takes place, as with the greater number of metallic salts. The only case of the production of a pure phosphuret by this process appears to be that of phosphuret of copper, which is thrown down whenever phosphuretted hydrogen is passed through solutions of the salts of that metal. (H. ROSE, *Poggend. Ann.*, xxiv. 320; and *Ann. Ch. et Ph.*, lxvi. 366.) The fused phosphurets have a metallic lustre; if they contain a difficultly-fusible metal, they are more fusible than the metal they contain; if an easily-fusible metal, less so. They are mostly crystallizable, and totally or partly decomposable at a high temperature. The greater number of the phosphurets have only been examined by Pelletier. (*Ann. de Chim.*, i. and xiii., and *Mémoires et Observations de Chimie.*) The existence of compounds of metallic oxides with phosphorus appears doubtful.

When phosphorus is introduced into the solutions of those metals which have but a feeble attraction for oxygen, it reduces them to the metallic state. Thus gold, silver, platinum, and copper are thrown down by immersing a stick of phosphorus into their respective solutions.

The *Hypophosphites* and the *Phosphites* have been imperfectly examined. When heated they evolve phosphorus or phosphuretted hydrogen, and are converted into phosphates: their solutions smell of phosphorus, and reduce the salts of gold, silver, and mercury. (p. 418.)

ACTION OF PHOSPHORIC ACID. The *metallic phosphates* may be formed either by dissolving the oxides in phosphoric acid, or by adding a solution of phosphoric acid, or of an alkaline phosphate, to solutions of those metals which form insoluble or difficultly-soluble phosphates. The greater number of the phosphates are decomposed and converted into phosphurets, by ignition with charcoal: and those containing volatile oxides are volatilized at high temperatures. The phosphates of ammonia, potassa, and soda, are soluble; but the greater number of these salts are difficultly soluble, and some insoluble in water: they are dissolved by phosphoric, nitric, and hydrochloric acids, and precipitated, generally without change, by ammonia. Those which are insoluble are mostly decomposed by boiling with carbonate of potassa. Several of the phosphates occur in the native state, constituting some beautiful but generally rare minerals.

Each of the hydrates of phosphoric acid forms its own salts. The monohydrated acid, PO_5HO , forming monobasic salts in which the HO is replaced by MO. The bihydrated phosphoric acid, $\text{PO}_5\text{2HO}$, forms salts in which the water is either replaced by 2MO , or by MOHO ; and the terhydrated acid, $\text{PO}_5\text{3HO}$, forms salts in which either the whole or part of the water is similarly replaced, producing salts represented by $\text{PO}_5\text{3MO}$, or $\text{PO}_5\text{2MOHO}$, or by $\text{PO}_5\text{MO2HO}$. It is obvious, that upon the binary theory of salts, none of the above acids contain PO_5 , or dry acid; but are respectively represented in their hydrated state as

hydracids $= \text{PO}_6 + \text{H}$, $\text{PO}_7 + \text{H}$, and $\text{PO}_8 + \text{H}$. So that the first class of the phosphates (metaphosphates) would have the formula $\text{PO}_6 + \text{M}$; the second class (or pyrophosphates) $= \text{PO}_7 + 2\text{M}$, or $\text{PO}_7 + \text{MH}$; and the third class (or common phosphates) $= \text{PO}_8 + 3\text{M}$, or $\text{PO}_8 + \text{M}_2\text{H}$, or $\text{PO}_8 + \text{M}_2\text{H}_2$. (See p. 423.)

ACTION OF CARBON. Carbon unites to very few of the metals; and of the metallic *carburets*, one only is of importance, namely, carburet of iron, which is contained in the varieties of cast-iron, and steel.

When some of the metallic cyanides, and certain of the salts of metallic oxides and organic acids are decomposed by heat, the residuary products appear to be, in some cases, true carburets; these, however, have been but imperfectly examined.

CARBONIC ACID unites with the greater number of the metallic oxides, and forms *carbonates*. The carbonates of the common metallic oxides are difficultly soluble or insoluble in water, and may be obtained therefore in the form of precipitates by adding solutions of the carbonates of ammonia, potassa, or soda to those of the respective metallic salts: they are more or less soluble in water saturated by carbonic acid; some of them are entirely, and others only partially, decomposed at a red heat; their decomposition in these cases being modified and facilitated by the presence of air or vapor. Carbonate of magnesia, for instance, loses the whole of its carbonic acid at a red heat; carbonate of potassa retains it; and bicarbonate of potassa loses one half and passes into the state of carbonate. Carbonate of lime may be intensely heated out of the contact of air and steam, without loss of carbonic acid; and when steam is passed over carbonate of potassa at a red heat, it also loses carbonic acid, and hydrate of potassa is formed. The carbonates are decomposed by nearly all the other acids, and are then distinguished by the effervescence that ensues on the escape of carbonic acid gas.

In the neutral carbonates the proportion of oxygen in the base is to that in the acid as 1 to 2. Carbonate of potassa, for instance, consists of 48 of potassa containing 8 of oxygen, and 22 of carbonic acid containing 16 (8×2) of oxygen. The formula, therefore, of the neutral carbonates is $\text{CO}_2 + \text{MO}$, or $\text{CO}_3 + \text{M}$. (See p. 467.)

Several of the carbonates occur as natural products, constituting an important class of minerals.

CYANOGEN combines with many of the metals, and forms compounds, which we call *cyanides*, or *cyanurets*. The compounds of the *cyanic acid*, or the *cyanates*, are so decomposed, either by the action of water, or the acids, that the cyanic acid is resolved into carbonic acid and ammonia, with no trace of hydrocyanic acid. (In reference to the cyanates, &c., see p. 507.)

Sulphocyanides and *Sulphocyanates* produce a characteristic red color when added to a solution of persulphate of iron.

THE ACTION OF BORON upon the metals has not been fully investigated.

THE BORATES of the alkalis are soluble; with other bases the boracic

acid mostly forms difficultly soluble or insoluble compounds, which are easily formed by adding solution of boracic acid, or a soluble borate to the metallic solution. The borates are generally decomposed in the humid way, by sulphuric, nitric, and hydrochloric acids; but, at a red heat, the boracic acid expels the more volatile acids from their basic compounds. The presence of this acid may in many instances be detected by digesting its compounds in sulphuric acid, evaporating to dryness, and boiling the residue in alcohol, which will then be found to burn with a characteristic green flame. (See *Boracic Acid*, p. 527.)

ACTION OF THE METALS UPON EACH OTHER. The metals may, for the most part, be combined with each other, forming a very important class of compounds, the *metallic alloys*. In the act of combination they generally evolve heat; thus, when platinum and tin-foil are fused together, there is vivid ignition; so, also, when melted zinc and copper are suddenly mixed in the proportions to form brass, the increase of heat is such as to vaporize part of the metal. Various processes are adopted in the formation of alloys, depending upon the nature of the metals. Many are prepared by simply fusing the two metals in a covered crucible; but if there be a considerable difference in the specific gravity of the metals, the heavier will often subside, and the lower part of the bar or ingot will differ in composition from the upper; this may be to a great extent prevented by agitating the alloy till it solidifies. Mr. Hatchett found that when an alloy of gold and copper was cast into bars, the moulds being placed perpendicularly, the upper part of the bar contained more copper than the lower (*Phil. Trans.*, 1803); and although copper and silver appear readily to combine, it is extremely difficult to form a bar of their alloy, of perfectly uniform composition throughout.

Where one of the metals is very volatile, it should generally be added to the other after its fusion; and if both metals be volatile, they may be sometimes united by distilling them together.

It has been a question whether alloys are to be considered as compounds, or as mere mixtures; but, in many cases, their properties leave little doubt of their being real compounds, and in some cases they are found to unite in definite proportions only; and it is not improbable that all the alloys contain definite compounds of the metals. It is observed by Berzelius, that the acidifiable metals have the greatest tendency to combine with those which produce salifiable bases, and that arsenic, antimony, and tellurium, form definite compounds analogous to sulphurets and phosphurets, which are not uncommon as ores. Among the artificial, as well as the natural alloys, there are many which are crystallizable, and the true compound may sometimes be separated from the mere mixture of the metal by its tendency to crystallize.

The principal characters of the alloys are the following; i. We observe a change in the ductility, malleability, hardness, and color. Malleability and ductility are usually impaired, and often in a remarkable degree: thus gold and lead, and gold and tin, form a brittle alloy. The alloy of copper and gold is harder than either of its component parts; and a minute quantity of arsenic added to copper renders it white.—ii. The specific gravity of an alloy is rarely the mean of its component parts, in some cases an increase, in others a diminution of density having

taken place, as shown in the following table from Thenard (*Traité de Chimie*, vol. i., p. 394):

Alloys possessed of greater specific gravity than the mean of their components.

Gold and Zinc
„ Tin
„ Bismuth
„ Antimony
„ Cobalt
Silver and Zinc
„ Lead
„ Tin
„ Bismuth
„ Antimony
Copper and Zinc
„ Tin
„ Palladium
„ Bismuth
„ Antimony
Lead and Bismuth
„ Antimony
Platinum and Molybdenum
Palladium and Bismuth

Alloys having a specific gravity inferior to the mean of their components.

Gold and Silver
„ Iron
„ Lead
„ Copper
„ Iridium
„ Nickel
Silver and Copper
Copper and Lead
Iron and Bismuth
„ Antimony
„ Lead
Tin and Lead
„ Palladium
„ Antimony
Nickel and Arsenic
Zinc and Antimony.

iii. The fusibility of an alloy is generally greater than that of its components. Thus platinum, which is infusible in our common furnaces, forms, when combined with arsenic, a very fusible alloy; and an alloy of certain proportions of lead, tin, and bismuth, is fusible at 212° , a temperature many degrees below the melting-point of its most fusible constituent.

iv. Alloys are generally more oxidizable than their constituents, taken singly; a property which is, perhaps, partly referable to the formation of an electrical combination. Where an alloy consists of two metals, the one easily and the other difficultly oxidizable, it may be decomposed by exposing it to the action of heat and air, the former metal being converted into an oxide: its last proportions, however, are often not easily separated, being protected by combination with the least oxidizable metal. An alloy of three parts of lead and one of tin is infinitely more oxidizable than either of its components, and easily burns at a dull-red heat.

v. The action of acids on alloys may generally be anticipated by a knowledge of their effects upon the constituent metals; but if a soluble metal be alloyed with an insoluble one, the former is often protected by the latter from the action of an acid. Thus, silver alloyed with a large quantity of gold, resists the action of nitric acid in consequence of the insolubility of the latter metal in that acid; and, in order to render it soluble, it is requisite that it should be made to form about a fourth part of the alloy, in which case the nitric acid extracts it, and leaves the gold in an insoluble film or powder.

In other cases a metal insoluble, or nearly so, in certain acids, *per se*, is taken up in considerable quantity when alloyed; thus platinum is insoluble in nitric acid, but its alloy with silver is to a certain extent soluble; and when a triple alloy of gold and silver with a little platinum is rolled out and digested in nitric acid, both the silver and the platinum

are taken up. Rhodium is insoluble in acids, but, when alloyed with copper or lead, the nitrohydrochloric acid dissolves it.

Various classifications of the metals have been adopted by chemical authors*, some dependent upon their *physical*, others upon their *chemical* properties. The former can scarcely be considered as adapted to chemical inquiry, and the latter involve numerous difficulties in consequence of the gradual transition of metals of one class into those of another. I shall consider the metals in the order in which they are set down in the following table, and which is nearly that of their respective attractions for oxygen, with the exception of the last division, which includes substances in part imperfectly examined, and from which, as already remarked, silicium is by some excluded.

I.	II.	III.	IV.	V.	VI.
1 Potassium	3 Manganese	15 Copper	24 Arsenic	30 Mercury	38 Glucium
2 Sodium	9 Iron	16 Lead	25 Molybdenum	31 Silver	39 Zirconium
3 Lithium	10 Zinc	17 Antimony	26 Chromium	32 Gold	40 Yttrium
4 Calcium	11 Tin	18 Bismuth	27 Vanadium	33 Platinum	41 Thorium
5 Barium	12 Cadmium	19 Uranium	28 Tungsten	34 Palladium	42 Alumium
6 Strontium	13 Cobalt	20 Titanium	29 Columbium	35 Rhodium	43 Silicium
7 Magnesium	14 Nickel	21 Cerium		36 Osmium	
		22 Lanthanum		37 Iridium	
		23 Tellurium			

* Berzelius divides the metals into two leading classes: 1. Bases of the alkalis and earths; 2. Bases of the oxides and acids. The former are distinguished by their low specific gravity, being either lighter, or but little heavier than water, and they are so easily oxidized as to decompose water at common temperatures: in this list he includes Kalium (Potassium), Natrium (Sodium), Lithium, Ammonium (the hypothetical base of ammonia), Barium, Strontium, Calcium, Magnium (Magnesium), Alumium, Beryllium (Glucium), Yttrium, and Zirconium. The second class he subdivides into, 1. Electro-negative metals; that is, such as in combination with oxygen have a greater tendency to form acids, than oxides or salifiable bases; these are Selenium? Arsenic, Chromium, Molybdenum, Wolframium (Tungsten), Antimony, Tellurium, Tantalum (Columbium), Titanium, Osmium, and Gold. 2. Electro-positive metals, or such as in combination with oxygen especially produce salifiable bases: these are Platinum, Iridium, Rhodium, Palladium, Silver, Mercury, Uranium, Copper, Bismuth, Tin, Lead, Cadmium, Zinc, Nickel, Cobalt, Iron, Manganese, Cerium. The metals of the two last divisions are all more than four times heavier than water, very few of them are oxidized at common temperatures either by air or water, and their oxides are reduced by charcoal at high temperatures, and by potassium at a moderate heat. See also Thenard (*Traité de Chimie*), and an essay on the action of the vapor of water, at high temperatures, on the metals and their sulphurets, by M. V. Regnault. (*Ann. de Ch. et Ph.*, Lxii. 337.) Gmelin arranges the metals as follows.

A. LIGHT METALS. Sp. gr. ranging between 0·860 and 5·000, distinguished by their powerful affinity for oxygen, many of them rapidly decomposing water at common temperatures: their oxides are mostly basic, one only partaking of an acid character; they form few hyper or sub-oxides. They are—

a. *Alkali metals*, forming with oxygen fixed alkalis: they decompose water with energy at 32°. Kalium, Natrium, Lithium, Baryum, Strontium, Calcium.

b. *Earth metals*, combining with oxygen to form *earths*: they slowly decompose water at common temperatures, mostly easily when warm, or by the help of an acid. Magnium, Cerium, Lanthanum, Yttrium, Glycium, Alumium, Thorium, Zirconium, Silicium.

B. HEAVY METALS. Their sp. gr. lies between 5·308 and 22·000; some are brittle, some malleable: many of them rival the light metals in their affinity for oxygen, while in others this affinity is remarkably feeble. Their combinations with oxygen are partly *heavy basic oxides*, partly *metallic acids*, *suboxides*, and *hyperoxides*. The heavy metals are—

a. *Common, not alone reducible*: and these:

a *Brittle*, and aa *difficultly fusible*: Titanium, Tantalum, Tungsten, Molybdenum, Vanadium, Chromium, Uranium, Manganese. ββ. *Easily fusible or volatile*. Arsenic, Antimony, Tellurium, Bismuth.

β. *Malleable*. Zinc, Cadmium, Tin, Lead, Iron, Cobalt, Nickel, Copper.

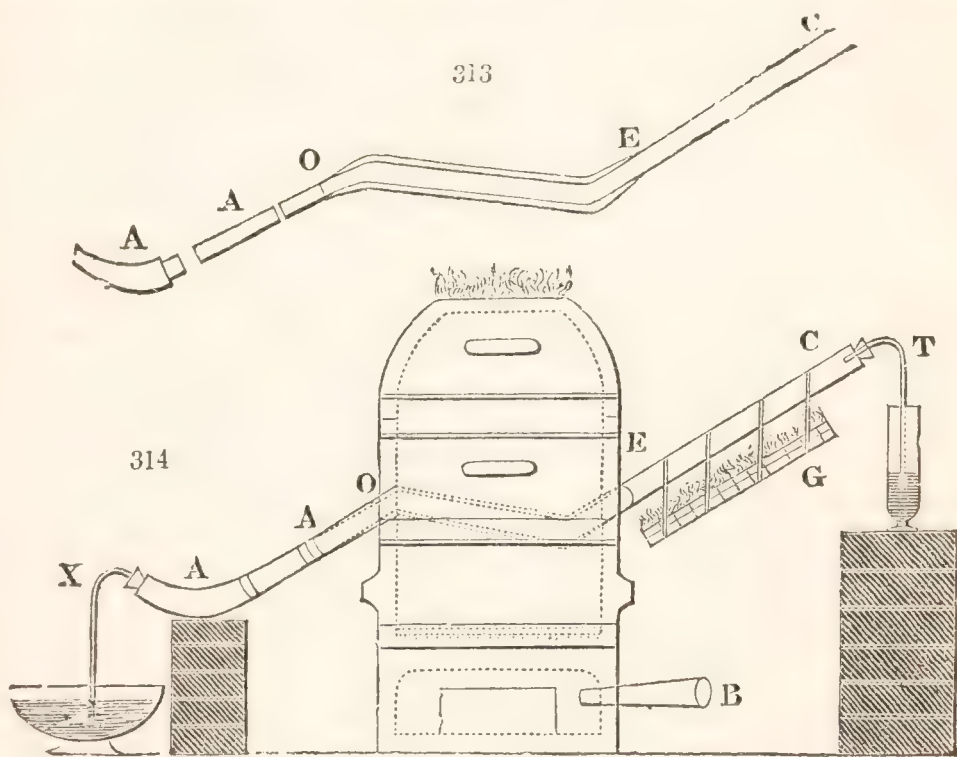
b. *Noble: reducible alone*. Mercury, Silver, Gold, Platinum, Palladium, Rhodium, Iridium, Osmium.

§ I. POTASSIUM. K. 40.

POTASSIUM (or Kalium of the German chemists) was discovered in 1807 by Sir Humphry Davy (*Phil. Trans.*, 1808). He obtained it by submitting hydrate of potassa, or caustic potash, to the decomposing action of Voltaic electricity: the metal was slowly evolved along with hydrogen at the negative pole. By this process, however, it could only be procured in very minute quantities, and other methods have since been devised. The following is that originally suggested by Gay Lussac and Thenard (*Recherches Physico-chymiques*), and is the first by which large quantities of potassium were obtained.

1. A sound and perfectly clean gun-barrel is bent, as shown in the annexed sketch (fig. 313). It is then covered with an infusible lute between the letters o and E, and the interior of the luted part is filled

with clean iron-turnings. Pieces of fused potassa are then loosely placed in the barrel between E and c. A A is a copper tube and small receiver, which are adapted to the extremity o, and to each other, by grinding. This apparatus is next transferred to the furnace, arranged as shown in fig. 314, x and T representing two glass tubes dipping into mercury.

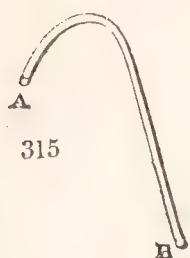


The furnace is supplied with air by a good double bellows entering at B, and a small wire basket, G, is suspended below the space EC.

The part of the barrel in the furnace is now cautiously raised to a white heat, and the escape of air by the tube x shows that all is tight. Some burning charcoal is then put at the end E, of the cage G, which causes a portion of potassa to liquify and fall into the lower part of the barrel upon the iron. Hydrogen gas instantly escapes by the tube x, and attention must now be had to keep the copper tubes A A cool, by laying wet cloths upon them. When the evolution of gas ceases, fresh charcoal is placed under the potassa, and so on till the whole has passed down; if too much potassa be suffered to fall at once, the extrication of gas at x will be very violent, which should be avoided. If the space between A and o should become stopped by potassium, gas will issue by the tube T (which must always be under a greater pressure of mercury than the tube x), and the potassium must be cautiously fused by applying hot charcoal to the copper tube, when the gas will again appear at x and cease at T. When the operation is concluded, the tubes x and T are removed, and corks quickly applied to the holes; and when the apparatus

is cool, the barrel is carefully removed from the furnace, and a little naphtha suffered to run through it. The potassium is found in globules in the tube and receiver *AA*, and considerable portions often lodge at *o*. The success of this operation is certain, if the heat has been sufficient: but the barrel, if not very carefully covered with lute, is apt to melt, and much, if not the whole, of the product is lost.

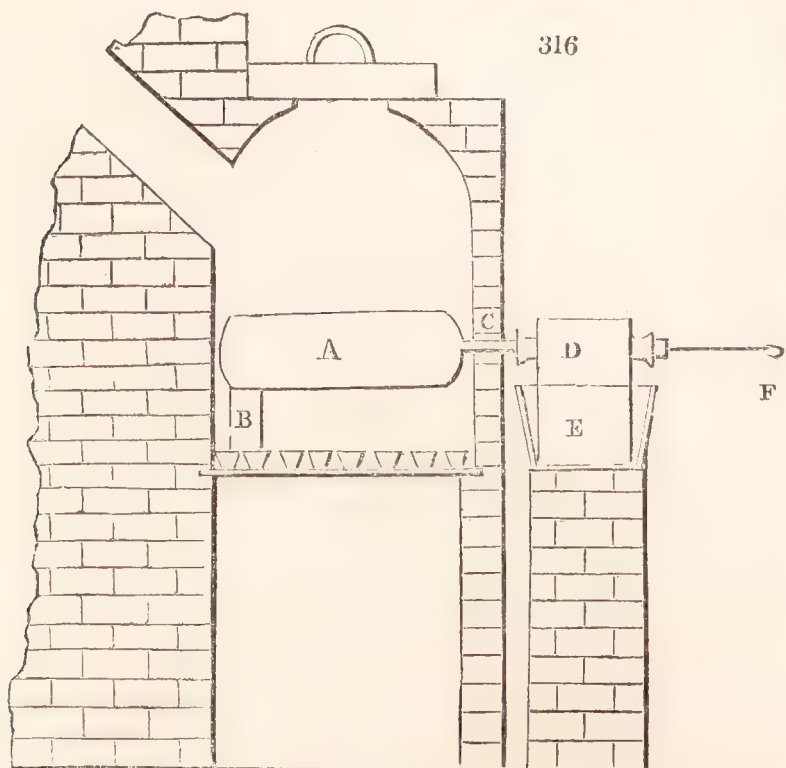
2. M. Brunner (*Quarterly Journal*, xv. 379) employs a spheroidal wrought-iron bottle, of a capacity between a pint and a quart, and a piece of gun-barrel of the annexed shape is fitted to its neck by grinding at the end *A*. When this bottle is charged and well luted it is placed in a proper furnace, nearly perpendicularly, and so that the greater part of the tube may be exposed to heat (it being protected by coils of iron-wire rolled round it), while the end



B projects, and has attached to it a copper receiver with a small safety-tube. This receiver, when in use, is about half filled with naphtha, and kept cold by ice or cold water. The bottle is charged with 4 ounces of fused caustic potassa, introduced, in small portions, alternately, with 6 ounces of clean iron-turnings broken in a mortar, and 1 ounce of powdered charcoal; and this mixture is covered by 2 ounces more of iron-turnings: it is then placed in a furnace, and a glass tube inserted into the protruding barrel at *B*. As soon as the whole acquires a bright red heat, inflammable gas is evolved, which burns with a violet flame, and shortly after the green vapour of potassium is seen in the glass tube, which is then removed, and the copper receiver substituted, so that the end *B* may dip into the naphtha. When the evolution of gas ceases, the fire is extinguished, and the receiver carefully removed. A very successful result furnished 150 grains of potassium, in small globular masses. In another experiment the mixture in the retort consisted of 8 ounces of pure and fused carbonate of potassa, 6 of iron-turnings, finely bruised, and 2 of charcoal: from these, 140 grains of potassium were obtained.

3. In Germany, where large quantities of potassium are obtained by the decomposition of potassa by carbon, crude tartar is resorted to as its

source, which is first calcined so as to be converted into an intimate mixture of charcoal and carbonate of potassa. Mitscherlich directs 6 lbs. of tartar to be ignited in a covered melting-pot till gases are no longer evolved, the product is then reduced to powder before it cools, and mixed with 10 ounces of common charcoal in very coarse powder. This mixture is put into a wrought-iron bottle *A*, fig. 316, (such as used for holding mercury), well luted exteriorly with a mix-



ture of sand and clay, and placed on its side in a wind-furnace, (supported by a fire-brick B,) a short iron tube c, as wide as the bottle will admit of, being fitted to it by grinding, to connect it with the copper receiver D E, which is half filled with naphtha, and provided with a tube for the escape of gas, and with the means of occasionally introducing an angular iron rod F, so as to cleanse the connecting tube should it become clogged. As first obtained, the potassium is impure, and partly perhaps in the state of a carburet; so that it generally requires to be purified by redistillation, which is performed in a small iron retort, the beak of which dips into naphtha: the process requires care, and is attended by the loss of more or less of the metal. (See, in reference to the details of this process, BERZELIUS' *Lehrbuch*, II. 51, *Ed.* 1844, Dresden.)

The theory of these operations is not clearly understood in its minute details. When pure hydrate of potassa is employed in the gun-barrel experiment, more than a fourth of its weight of potassium is never obtained; the remainder is chiefly found partly undecomposed and partly in combination with the produced oxide of iron, forming a hard brittle compound, difficultly acted on by water. A grey pulverulent compound of carbonic oxide and potassium is also at the same time formed. The evolution of potassium is in this case dependent upon the attraction of the iron at a high heat for oxygen; the water of the potassa is at the same time decomposed, and possibly the nascent hydrogen may perform its part in the reduction; the readiness with which potassium assumes the elastic state at high temperatures also contributes to its evolution.

In the process in which carbon and carbonate of potassa are used, the carbon deoxidizes both the carbonic acid and the oxide of potassium, forming carbonic oxide, which is evolved during the operation; the above mentioned grey compound is also at the same time produced. This substance by the action of water yields peculiar combinations, which will be described further on as *oxicarburets of potassium*, (p. 591.) A black substance is also sometimes formed in these operations, the composition of which has not been determined, but which is probably a carburet of potassium: it is dangerously explosive, and often detonates when touched by a hard or sharp substance: it seems also sometimes to be formed when impure potassium is fused under naphtha, especially if the operation be performed at too high a heat. Potassium may be fused and obtained in beautifully brilliant globules by heating it in melted tallow; but if in this process the temperature be too high the mixture blackens, inflames, and explodes, especially if it be stirred with the view of collecting the scattered globules into one mass, so that these operations require caution in their performance.

Potassium is a bluish-white metal of great lustre. It instantly tarnishes by exposure to air, and is gradually converted into an oxide; but, according to Bonsdorff, in air which is perfectly free from moisture and carbonic acid, it retains its lustre. At 60° it is malleable, and of the consistency of wax. Its specific gravity is about 0.865. It is most conveniently preserved in naphtha, either by immersing it in that liquid, or by dipping the pieces of metal into it, and keeping them thus varnished, in a small well-stopped phial. When used, the exterior must be wiped with blotting-paper, or scraped; or the naphtha may be driven off by a gentle heat. At 150° it enters into perfect fusion; and at a bright red

heat, in close vessels, it boils, and rises in green vapor. At 32° it is a hard and brittle solid, of a crystallized texture. If heated in air, it burns with a brilliant purple flame. It is an excellent conductor of electricity and of heat, and its lustre is well shown by fusing it under tallow or naphtha, through which it is seen as brilliant as mercury; or by flattening a clean globule of it by pressure between two pieces of plate glass.

POTASSIUM AND OXYGEN. There are three oxides of potassium, namely, a *suboxide* $=K_2O$, a *protoxide* $=KO$, which in the state of *hydrate* constitutes *caustic potassa* $=KO,HO$, and a *peroxide* $=KO_3$.

SUBOXIDE OF POTASSIUM. K_2O , is formed by heating potassium in a limited portion of air, the oxygen of which is insufficient for its conversion into protoxide: it is also formed by heating 1 part of potassium with $1\frac{1}{2}$ of hydrate of potassa; while hot it is reddish, but grey when cold: it is very fusible and inflammable, taking fire when gently heated, and burning into peroxide. Water converts it without combustion into potassa, hydrogen being evolved. At a white heat out of contact of air potassium is volatilized, and protoxide remains. (H. DAVY. G. LUSSAC and THENARD. BERZELIUS.)

PROTOXIDE OF POTASSIUM. ANHYDROUS POTASSA. KO . Anhydrous potassa is most readily obtained by heating 1 atom of potassium, $=40$ with 1 of hydrate of potassa $=57$: hydrogen is evolved, and 2 atoms of protoxide are formed. ($K + KO,HO = 2KO + H$.) When 1 atom of potassium acts upon 1 atom of water out of the contact of air, it is also produced. ($K + HO = KO + H$.) When peroxide of potassium is intensely heated, it loses oxygen and leaves protoxide. (H. DAVY.) It is a hard grey brittle substance, fusible at a bright red heat, sp. gr. about 2.65: extremely caustic and alkaline.

The composition of this oxide is learned by the action of potassium upon water: when the metal is thrown upon water, or even upon ice, it inflames with the evolution of hydrogen, and burns into a small globule of fused potassa, which, in combining with water, produces so much heat as to cause a slight explosion. If the potassium be plunged under water the decomposition ensues with explosive violence, but by carefully employing small quantities of the metal, or by previously amalgamating it with mercury, the experiment may be so conducted as to collect the evolved hydrogen, which thus becomes the indicator of the quantity of oxygen taken by the potassium, 100 parts of which are thus found to combine with 20 of oxygen: and $20 : 100 :: 8 : 40$, so that the equivalent of potassium thus deduced is 40. The equivalent deduced from other sources fluctuates between 39 and 40, the average of the closest experiments giving the fraction nearest to the latter number, oxygen being $=8$. I have therefore retained 40 as the equivalent of potassium upon the hydrogen scale. (39.3 GRAHAM, 39.15 TURNER, 39.2 L. GMELIN, 39.08 PENNY.) The composition of anhydrous potassa is therefore

					Gay Lussac		Davy.	
					Berzelius.	and Thenard.		
Potassium	1	40	83.33	83.371 85
Oxygen	1	8	16.95	16.629 15
Potassa.....	1		48		100.00	100.00	100.000	100

HYDRATED PROTOXIDE OF POTASSIUM. CAUSTIC POTASSA, KO, HO , is usually procured by decomposing carbonate of potassa by lime. The process consists in boiling in a clean iron vessel pure carbonate of potassa, with half its weight of pure quicklime, in 8 or 10 parts of water. The lime, which may be previously slaked, is gradually added to the boiling alkaline solution, which is kept constantly stirred, and towards the end of the operation it is tested by filtering a small portion, and pouring it into three or four times its bulk of dilute nitric acid; if there be no effervescence, sufficient lime has been used; but if carbonic acid escapes, the ebullition with lime must be continued, taking care to keep up the original quantity of water, until the tested portion shows no signs of carbonic acid. The whole is then allowed to remain quiet, that the carbonate of lime and excess of the hydrate of lime may subside; the clear liquor or *ley* may then be siphoned or poured off, concentrated by evaporation, strained through a clean calico filter, and set by in a well-stopped bottle till it admits of being decanted from any sediment. The clear solution is to be evaporated in a polished iron or pure silver vessel till it assumes the appearance of an oily liquid, and concretes on cooling. (It is often cast into sticks for the use of surgeons, who employ it as a caustic; in this state it generally contains some peroxide and other impurities, and evolves oxygen and deposits a sediment when dissolved in water.) It is the *potassa fusa* of the *London Pharmacopœia*; the *Lapis infernalis* of old pharmacy. Having obtained it in this state it is sometimes further purified by boiling it in a silver basin with highly-rectified alcohol for a few minutes, and then setting it by in a stopped phial; when the impurities are deposited the alcoholic solution may be poured off and rapidly evaporated to dryness in a silver vessel; or if the quantity of alcohol be considerable, it may be distilled off in a silver alembic with a glass head: the heat may then be raised so as to fuse the potassa, which on cooling should be broken up and preserved in well-closed phials: if, however, pure materials and due care be employed, the alcoholic purification may be dispensed with, inasmuch as when so prepared the product always contains traces of carbonate, and sometimes of acetate of potassa.

Caustic potassa may also be obtained by decomposing sulphate of potassa by baryta: pure crystallized sulphate of potassa in fine powder is added to concentrated baryta-water; sulphate of baryta falls, and potassa remains in solution; equivalent proportions must be carefully adhered to, or only a very slight excess of baryta left, which falls as carbonate during the evaporation of the clear decanted liquor*.

Hydrate of potassa consists of

						Berzelius.	Gay Lussac.	Berthollet.			
Potassa	1	48	84.21	84	81.55	86.36
Water	1	9	15.79	16	18.45	13.64
<hr/>											
Hydrate of potassa	1		57		100.00		100		100.00		100.00

* As potassa is generally, and indeed almost exclusively procured from vegetables, it was formerly called *vegetable alkali*: but it also exists in certain minerals, and in a few animal secretions. Fuchs says that it may be economically obtained from cer-

tain varieties of felspar: for this purpose they are calcined with lime, then left for some time in contact with water, and the liquor filtered and evaporated. He says he has thus procured 19 *per cent.* from felspar and 15 from mica.

Hydrate of potassa is white and somewhat crystalline in texture: its sp. gr. 1.7. (2.1 DALTON.) It is very acrid and corrosive, fusible at a heat below redness, and evaporates from an open vessel, at a bright-red heat, in the form of acrid fumes. A platinum wire, dipped into potassa and heated by the blowpipe, communicates a characteristic violet tint to the flame. At a white heat it is decomposed by charcoal, and carburetted hydrogen, carbonic oxide, and potassium, are formed. It quickly absorbs moisture and carbonic acid from the air, and is soluble in half its weight of cold water. When reduced to powder and slightly moistened it forms a crystallized combination which is said to be a *terhydrate*; $\text{KO}, 3\text{HO}$. By keeping a strong aqueous solution of potassa at a low temperature in a stopped phial, octohedral and tabular crystals may be obtained which are stated to be a definite *pentahydrate*; $\text{KO}, 5\text{HO}$. (P. WALTER, *Poggend.*, xxxix. 192.)

It is highly alkaline, powerfully reddening turmeric, and converting several vegetable blues to green: and by a strong solution of it these colors are almost destroyed. It also acts energetically upon the greater number of organic products, and unites with the fat oils to form soap, hence the term *soap-lye*, applied to its aqueous solution.

When touched with moist fingers caustic potassa has a soapy feel, in consequence of its action upon the cuticle, and it then exhales a peculiar odor; this is also perceptible in the solution of potassa, and is probably referable to the formation of ammonia, arising from traces of organic matter accidentally present. In the fused state it produces heat when dissolved in water; but in its crystallized state it excites considerable cold, especially when mixed with snow. At a natural temperature of 30° , Lowitz found that equal weights of crystallized potassa and snow depressed the thermometer 45° . (*Ann. de Chim.*, xxii.) It dissolves sulphur and several sulphurets, and alumina and silica. The oxides of manganese, zinc, tin, lead, antimony, cobalt, arsenic, molybdenum, tungsten, and nickel, are also soluble in aqueous solution of potassa.

The *Liquor Potassæ* of the London Pharmacopœia is directed to be prepared as follows: "Take of carbonate of potassa 15 ounces, lime 8 ounces, boiling distilled water a gallon. Dissolve the carbonate in half a gallon of the water; sprinkle a little of the water upon the lime in an earthen vessel, and the lime being slaked add the rest of the water. The liquors being immediately mixed together in a close vessel, shake them frequently until they are cold; then set the mixture by that the carbonate of lime may subside. Lastly, having poured off the supernatant liquor, keep it in a well-stoppered green glass bottle." Its specific gravity is 1.063. There is some difficulty in preserving this aqueous solution of potassa, for if kept in a corked bottle the cork is soon acted on and decayed; and if a bottle with a glass stopper be used, the stopper is apt to become immovably fixed.

When a solution of caustic potassa is required to be filtered, it is very apt both to act upon the filter and to absorb carbonic acid from the air, so that filtration should in all cases as far as possible be avoided, and the liquor obtained clear by subsidence: on the large scale linen strainers are generally used; upon the small scale the absorption of carbonic acid may be prevented, by covering the funnel with a plate of glass, and receiving it into a bottle as nearly air-tight as possible; the annexed filtering

apparatus, (fig. 317,) contrived by Mr. Donovan (*Ann. of Philosophy*, xxvi. 115), may also sometimes be used. It consists of two glass vessels connected by a tube, made air-tight by perforated corks at the junctions *a* and *b*. The upper vessel containing the solution to be filtered, terminates in a conical pipe, ground into the lower one, and into which is stuffed a piece of coarse linen. But in most cases filtration may be dispensed with, and the solution of potassa obtained clear by mere subsidence.

In all cases where solution of potassa is employed, it must be recollected that it gradually acts upon glass, especially upon flint glass, which abounds in oxide of lead; hence green glass vessels are preferable; but where the alkaline solution is to be exposed to heat, or evaporated to dryness, even these communicate some impurity, and in such cases vessels of pure silver can only be relied upon, for almost all other metals, platinum not excepted, are more or less acted upon.

The solution of caustic potassa is frequently impure from the presence of carbonic acid, silica, alumina, lime, and sulphuric or hydrochloric acid. If nitric acid cause an effervescence when dropped into it, it indicates *carbonic acid*; if a gelatinous precipitate, not soluble in very slight excess of acid, it is *silica*; if soluble, it is *alumina*. The presence of *lime* is shown by adding oxalate of ammonia to the solution previously neutralized by nitric acid: in the same solution nitrate of silver will indicate hydrochloric acid, or *chlorine*, and nitrate of baryta, *sulphuric acid*, or *sulphates*.

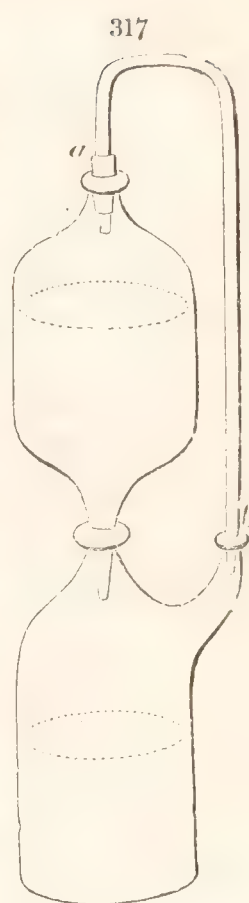
It may sometimes be useful to know the quantity of real potassa contained in watery solutions of different specific gravities; the following are the results of Dalton's experiments, in reference to this question:

Specific Gravity.	Potassa per Cent.	Boiling-Point.	Specific Gravity.	Potassa per Cent.	Boiling-Point.
1.68	51.2	329°	1.33	26.3	229°
1.60	46.7	290	1.28	23.4	224
1.52	42.9	276	1.23	19.5	220
1.47	39.6	265	1.19	16.2	218
1.44	36.8	255	1.15	13.	215
1.42	34.4	246	1.11	9.5	214
1.39	32.4	240	1.06	4.7	213
1.36	29.4	234			

PEROXIDE OF POTASSIUM. KO_3 . When potassium is burned with free access of air, or in oxygen gas, a yellow fusible substance is obtained, which, on cooling, acquires a scaly crystalline appearance. It consists of

					Gay Lussac and Thenard.	
Potassium	1	40	62.5	65		
Oxygen	3	24	37.5	35		
Peroxide of potassium	1	64	100.0	100		

This substance has some singular properties; it supports the combustion of most of the inflammables, and when heated in hydrogen, diminishes the bulk of the gas, and forms water: it decomposes ammonia under the



same circumstances. When put into water, oxygen gas is evolved, and a solution of potassa obtained. When hydrate of potassa is fused in an open crucible, a portion of its water is disengaged, and oxygen absorbed, so as to form this peroxide; and hence it is, that common caustic potassa almost always effervesces, and gives out oxygen upon the affusion of water. When potassium is dropped into melted nitre, the peroxide is also formed; likewise by passing oxygen over potassa heated to redness.

POTASSIUM AND CHLORINE. CHLORIDE OF POTASSIUM. KCl . Potassium burns brilliantly in chlorine, especially if introduced into the gas in the state of fusion, as, otherwise, a crust of chloride is apt to form and protect the interior from further action. This compound, formerly called *muriate of potash*, consists of

Potassium.....	1	40	52.6	Ure. 53
Chlorine	1	36	47.4	47
<hr/>							
Chloride of potassium	1		76		100.0		100

When potassium is heated in gaseous hydrochloric acid, chloride of potassium is formed, and hydrogen evolved; an experiment already adverted to under the article *Hydrochloric Acid* (p. 315). It is also formed by dissolving potassa or its carbonate in hydrochloric acid, and evaporating to dryness. The affinity of potassium for chlorine exceeds even that for oxygen; so that potassa heated in chlorine loses oxygen (and water), and yields chloride of potassium: hence, also, potassium heated with other chlorides, evolves their bases and forms chloride of potassium. When chlorine is passed over iodide of potassium at a red heat, iodine is expelled, and chloride of potassium formed.

Chloride of potassium dissolves in three parts of water at 60° , or, according to Gay Lussac, 100 parts water at 32° dissolve 29.23, and for every 1.8° above 32° , the water takes up 0.2738 more of the salt. One part of the powdered salt stirred into four parts of cold water produces a depression of temperature of between 20° and 25° , whereas chloride of sodium under the same circumstances only depresses the thermometer between 2° and 3° ; hence it has been proposed to estimate the relative proportions of these chlorides when mixed, by the depression of temperature resulting from their solution. Chloride of potassium crystallizes in cubes, which are anhydrous; its taste is saline and bitter. Its sp. gr. 1.9. In old pharmacy it was called *digestive salt of Sylvius*; also, *regenerated sea-salt*. It is insoluble in alcohol. When intensely heated in open vessels, it evaporates in the form of white fumes. This salt is a residue of several chemical and pharmaceutical processes, and is sometimes found in considerable quantities in rough salt-petre, where it is often mistaken for common salt; it is also contained in kelp: the manufacturers of alum occasionally employ it as the source of potassa in that salt.

When a warm solution of chloride of potassium is mixed with perchloride of iodine, gold-colored prismatic crystals are formed, very soluble in water, and immediately decomposed by ether, which abstracts the iodide of chlorine. The formula of the crystals is KCl, ICl_3 . (FILHOL. *Journ. de Pharmacie*, xxv.)

HYPOCHLORITE OF POTASSA. KO,ClO . This salt, called also *chloride of potassa*, and *chlorinated potassa*, has only been obtained in solution by adding aqueous hypochlorous acid to solution of potassa. When chlorine is passed into solution of carbonate of potassa so as not quite to saturate the alkali, bicarbonate of potassa is at first formed, which crystallizes out of the solution: upon the further action of chlorine carbonic acid is evolved, and a solution of hypochlorite of potassa is obtained, provided the liquor be kept cold. If heated, or if more than 1 atom of chlorine to 1 of potassa be used, the hypochlorite is decomposed, and part of the bleaching power of the solution destroyed. A solution of hypochlorite of potassa is also obtained by double decomposition when solution of hypochlorite of lime is mixed with carbonate of potassa. It is colorless, powerfully bleaching, and antiseptic. When chlorine is passed over slightly moistened carbonate of potassa, a bleaching salt mixed with bicarbonate of potassa is obtained.

HYPOCHLORATE OF POTASSA. KO,ClO_4 . **CHLORITE OF POTASSA.** KO,ClO_3 . When a solution of potassa is saturated by peroxide of chlorine (hypochloric acid) and evaporated in vacuo, crystals resembling chlorate of potassa are formed, but which when acted upon by a mixture of 1 part of sulphuric acid and 10 of water, give off peroxide of chlorine with effervescence. The crystals are decomposed by carbonic acid: they deliquesce in moist air. (MARTENS, *Ann. Ch. et Ph.*, lxi. 293.) According to Millon, peroxide of chlorine gives with solution of potassa, chlorate and chlorite of potassa. $2\text{ClO}_4 + 2\text{KO} = \text{KO},\text{ClO}_5 + \text{KO},\text{ClO}_3$.

CHLORATE OF POTASSA, KO,ClO_5 or K,ClO_6 , is formed by passing excess of chlorine through a solution of potassa; chloride of potassium is one of the results, the other is *chlorate of potassa*, a salt in brilliant rhomboidal tables (formerly called *oxymuriate of potash*). Its crystalline forms have been described by Levy (*Quarterly Journal*, xv. 286), and by Brooke (*Ann. Phil.*, v. 451): they belong to the oblique prismatic system.

This salt is prepared, upon the large scale, by charging one or two Woulfe's bottles with a strong solution of pure carbonate of potassa, and passing chlorine slowly through it. The gas is absorbed, and the liquor effervesces, chiefly from the escape of carbonic acid; when this has ceased the liquor may be put aside in a cold dark place for about 24 hours, when it will be found to have deposited a considerable portion of the crystallized chlorate, which may be taken out, drained, and purified by solution in hot water, which, during cooling, again deposits the salt in white crystalline scales. The mother-liquor, from which more of the salt may be obtained by evaporation, is often of a pinkish tint, from the presence of a trace of manganese; but this disappears when sufficiency of chlorine has been passed in to saturate it, and it acquires a brownish hue. Solution of pure potassa absorbs the gas more readily than the carbonate, but nearly with the same phenomena, and in either case care must be taken that the tube conveying the chlorine does not become stopped up by the salt, which is apt to happen if it be not sufficiently capacious.

The action of chlorine upon a solution of carbonate of potassa at first produces bicarbonate of potassa, which, by the continued action of chlo-

rine, is decomposed, the whole of the carbonic acid expelled, and *hypochlorite of potassa* and *chloride of potassium* are then formed; $6\text{KO} + 6\text{Cl} = 3\text{KCl} + 3[\text{KO}, \text{ClO}]$: the hypochlorite is itself afterwards resolved into chlorate of potassa and chloride of potassium; $3[\text{KO}, \text{ClO}] = \text{KO}, \text{ClO}_5 + 2\text{KCl}$: so that the ultimate result may be thus represented: $6\text{KO} + 6\text{Cl} = 5\text{KCl} + \text{KO}, \text{ClO}_5$.

According to Löwig, chloride of lime, which, by long keeping, has lost much of its bleaching power, contains chlorate of lime, and may be used for the preparation of chlorate of potassa: the solution of the lime salt is boiled in order to complete the conversion of the chlorite into chlorate, and then partially decomposed by carbonate of potassa, or evaporated with an admixture of chloride of potassium, when chlorate of potassa crystallizes, and chloride of calcium remains in solution. (GRAHAM.)

According to Graham (*Proc. Chem. Soc.*, I.), the following is the most economical process for the preparation of this chlorate. One equivalent of carbonate of potassa and one of hydrate of lime are mixed and exposed to a current of chlorine; the mass becomes hot and evolves water during the absorption of the gas: when saturated, it is gently heated to complete the decomposition. No oxygen is evolved, the action being such that $6[\text{KO}, \text{CO}_2]$ and $6[\text{CaO}, \text{HO}]$, acted on by 6Cl , yield $5\text{KCl} + 6[\text{CaO}, \text{CO}_2] + \text{KO}, \text{ClO}_5$; whilst 6HO are evolved. By the action of water the soluble salts are separated from the carbonate of lime, and the chloride of potassium and chlorate of potassa by crystallization.

Chlorate of potassa is an anhydrous salt of a cooling and austere taste. It forms tabular crystals of a pearly lustre, belonging to the oblique prismatic system. (BROOKE, *Ann. Phil.*, xxi. 451. HAIDINGER, *Edin. Jour. Sc.*, I. 103.) Its specific gravity is 1.989. (HASSENFRATZ.) When pure, its aqueous solution is not rendered turbid by nitrate of silver. When triturated, it appears phosphorescent. It decrepitates and fuses at a temperature between 400° and 500° : at a higher heat it effervesces, and gives out nearly 40 *per cent.* of its weight of oxygen, and chloride of potassium remains. (As a source of oxygen gas it has already been adverted to, and the extraordinary facility of its decomposition by heat when mixed with a little oxide of manganese (p. 270) has been mentioned: see also *perchlorate of potassa*.) It is soluble in 18 parts of cold and 2.5 of boiling water; or, according to Gay Lussac, 100 parts of water at 32° dissolve 3.5 parts, at 59° 6 parts, at 95° 12 parts, at 120° 19 parts, and at 216° , which is the boiling-point of the saturated solution, 60 parts. It is soluble in 120 parts of alcohol, sp. gr. .840, at 60° . It acts very energetically upon many inflammables, and triturated with sulphur, phosphorus, and charcoal, produces inflammation and explosion. A mixture of three parts of this chlorate with one of sulphur, detonates loudly when struck upon an anvil with a hammer, and even sometimes explodes spontaneously; hence it should not be kept ready mixed. Chlorate of potassa was proposed by Berthollet as a substitute for nitre in gunpowder. The attempt was made at Essone, in 1788; but, as might have been expected, no sooner was the mixture of the chlorate with the sulphur and charcoal submitted to trituration, than it exploded with violence, and proved fatal to several persons. With phosphorus the detonation is dangerously violent; the experiment is best made, by wrap-

ping a grain of phosphorus and two of the chlorate in a small piece of paper, and striking them a blow with a hammer, upon an anvil. The phosphorus is generally thrown about in an inflamed state. These phenomena depend upon the sudden decomposition of the chloric acid.

The action of sulphuric acid upon chlorate of potassa has already been adverted to (p. 279). If, instead of distilling the yellow mixture of the acid and chlorate with the caution there described, it be heated to about 212° , it suddenly explodes. The theory of this action is more explicitly described in the next article.

When sulphuric acid is dropped upon mixtures of this salt and combustibles, instant ignition ensues in consequence of the evolution of peroxide of chlorine. A mixture of sugar and the chlorate thus treated, is immediately kindled, with a red and blue flame; and a mixture of sulphuret of antimony and the salt suddenly deflagrates with a bright puff of flame and smoke: the latter mixture requires to be cautiously made, as it often takes fire by gentle trituration. Matches tipped with some of these inflammable mixtures, and called *Lucifers*, are now in common use, and are inflamed either by friction, or by the contact of sulphuric acid, which is most conveniently applied by putting some asbestos into a small well-stopped phial, and moistening it with sulphuric acid; the match is rapidly dipped into the phial and inflames on touching the asbestos, without the risk of spirting about the acid. Some of the matches which inflame by a pinch or blow, contain a portion of a drop of sulphuric acid hermetically sealed in a piece of very small and thin glass tube, and which escapes when broken, and acts upon the inflammable mixture. Berzelius gives the following as the best composition for the match: 30 parts of powdered chlorate of potassa, 10 of powdered sulphur, 8 of sugar, 5 of gum-arabic, and a little cinnabar. The sugar, gum, and salt, are first rubbed together into a paste with a sufficiency of water; the sulphur is then added, and the whole being thoroughly beaten together, small brimstone matches are dipped in, so as to retain a thin coat of the mixture upon their sulphuretted points: they should be quite dry before they are used. The recently improved lucifer-matches contain phosphorus, and inflame by slight friction upon emery-paper or any hard rough substance; so that the inconvenient use of oil of vitriol is entirely superseded. One of the compounds occasionally employed in percussion gun-locks is a similar composition: 10 parts of gunpowder are rubbed with water, and the soluble part poured off; the remaining paste is then mixed with $5\frac{1}{4}$ parts of finely-powdered chlorate of potassa, and a drop of it put into each of the small copper caps adapted to the peculiar tubular touch-hole of the gun; a blow being struck upon the cap the powder is inflamed, and communicates to that in the barrel. The great disadvantage of this compound is, that it forms products which soon rust the touch-hole and surrounding parts; fulminating mercury is, therefore, now generally substituted. When pure nitric acid acts upon chlorate of potassa, no oxide of chlorine is formed, but, on applying heat, chlorine and oxygen are evolved, and nitrate and perchlorate of potassa formed. (PENNY.) $4[\text{KO}, \text{ClO}_5] + 3\text{NO}_5 = 3[\text{KO}, \text{NO}_5] + \text{KO}, \text{ClO}_7 + 3\text{Cl} + 13\text{O}$. Dilute nitric acid does not decompose chlorate of potassa, even at a boiling heat. When chlorate of potassa and iodine are heated together, chloride of iodine is evolved, and chloride of potassium and chlorate and iodate of

potassa are formed. (WÖHLER.) Iodine added to a boiling solution of chlorate of potassa, at first dissolves without color, but a further quantity of iodine renders it yellow and brown, iodate of potassa and chlorides of iodine being formed. (MILLON.)

The action of hydrochloric acid upon this salt is attended by the evolution of Davy's *euchlorine*, or, according to Millon, of chlorine and peroxide of chlorine. $\text{ClO}_5 + \text{HCl} = \text{ClO}_4 + \text{Cl} + \text{HO}$.

When sulphuric or nitric acids are poured upon mixtures of chlorate of potassa and certain combustibles under water, by means of a long funnel, inflammation also ensues. In this way a beautiful experiment may be made with phosphorus, a few small pieces of which are put at the bottom of a tall glass of water, and a little of the chlorate thrown in upon it; sulphuric acid is then carefully introduced into the contact of the salt, by a funnel with a tube long enough to reach to the bottom of the glass; the phosphorus presently inflames and burns vividly in different parts of the fluid, forming a kind of well of fire. A few grains of chlorate of potassa put into a teaspoonful of hydrochloric acid, and then diluted with water, form an extemporaneous bleaching-liquor.

Chlorate of potassa has been used in medicine as a means of imparting oxygen to the system, but Wöhler has shown that it passes off undecomposed, by the kidneys. It has been recommended by Dr. Stevens (*On the Blood*, p. 296), as a remedy in fever, cholera, and other malignant diseases supposed to arise from deficiency of saline matter in the blood; but as he always administered it in conjunction with other salts, the abstract merits of the chlorate remain doubtful, and have probably been overrated. The ultimate elements of chlorate of potassa are

Oxygen	6	48	38·71
Chlorine	1	36	29·03
Potassium	1	40	32·26
	<hr/>		<hr/>		<hr/>
	1		124		100·00

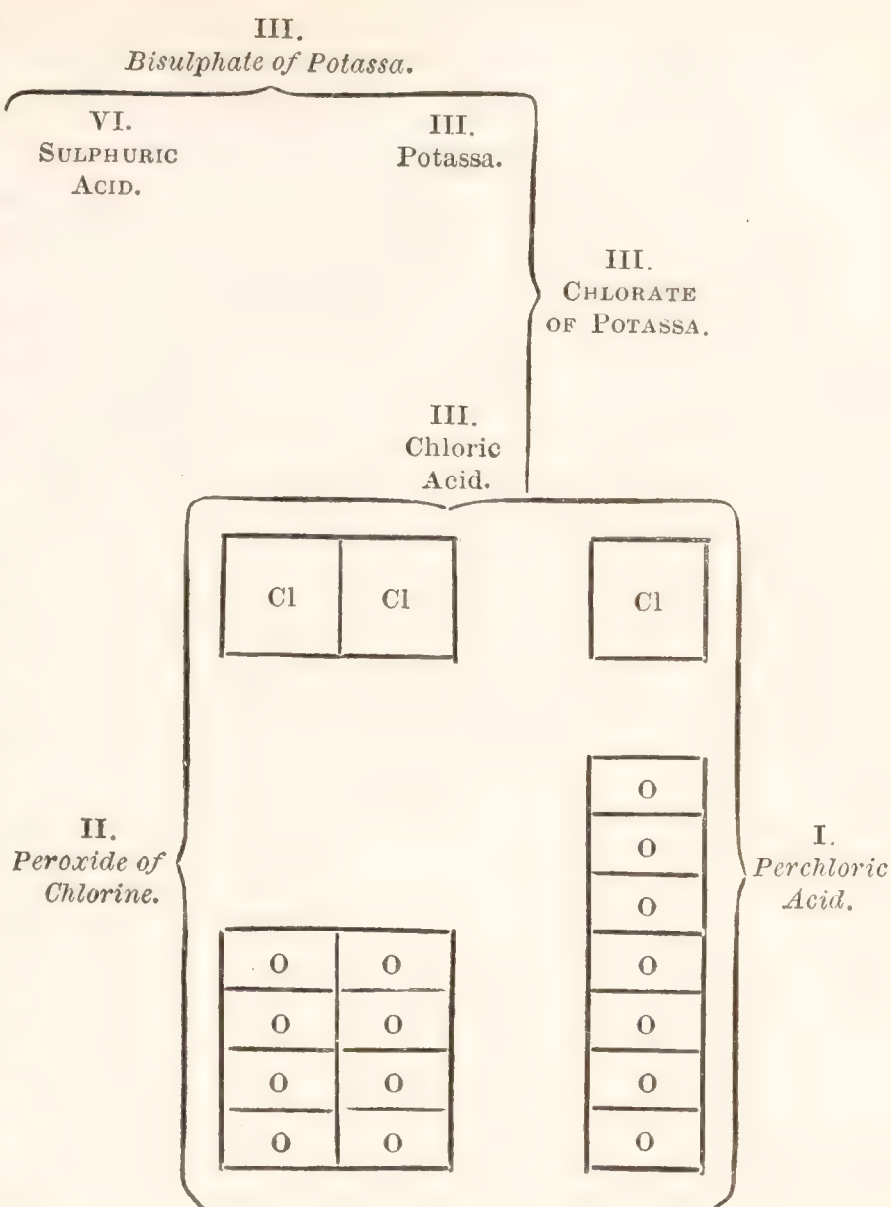
Or it consists of

Potassa	1	48	38·70	Berzelius. 38·49
Chloric acid	1	76	61·30	61·51
	<hr/>		<hr/>		<hr/>		<hr/>
Chlorate of potassa	1		124		100·00		100·00

PERCHLORATE OF POTASSA. **OXICHLORATE OF POTASSA.** KO, ClO_7 , or K, ClO_8 . This salt is formed when chlorate of potassa is heated in a porcelain crucible till it fuses and, giving out a portion of oxygen, becomes thick and pasty: the cooled mass, dissolved in hot water, deposits perchlorate of potassa on cooling, which may be purified by recrystallization. The chloride of potassium and undecomposed chlorate remain in solution. The action of heat on 2 equivalents of the chlorate forms 1 of chloride of potassium, and 1 of perchlorate; while 4 of oxygen are evolved. $2[\text{KO}, \text{ClO}_5] = [\text{KCl} + \text{KO}, \text{ClO}_7] + 4\text{O}$.

Perchlorate of potassa is also formed by moistening one part of chlorate of potassa with three of sulphuric acid, and subsequently *carefully* warming the mass till it becomes white, and the oxide of chlorine is expelled: in this state it consists of bisulphate and perchlorate of potassa, which may be separated by solution and crystallization, the former being much more soluble in cold water than the latter salt.

(In reference to the production of peroxide of chlorine and perchloric acid, as the result of the action of sulphuric acid upon chlorate of potassa, the annexed diagram may, perhaps, be useful. The original substances are printed in capitals, the components in common type, and the resulting compounds in italics; the volumes of oxygen and of chlorine being shown by the usual symbols of bulks which I have elsewhere employed. The Roman numerals denote the number of proportionals or equivalents presumed to be employed or formed.)



Thus it appears that 6 atoms of sulphuric acid acting upon 3 of chlorate of potassa form 3 of bisulphate of potassa, and detach 3 of chloric acid, the elements of which are 3 of chlorine and 15 of oxygen: of these, 2 atoms of chlorine and 8 of oxygen form 2 of peroxide of chlorine; and the remaining 1 of chlorine and 7 of oxygen form perchloric acid. If instead, as in the above diagram, of considering the mere formation of perchloric acid, we refer to the formation of perchlorate of potassa, we must assume that the oxygen is transferred to the chloric acid of an undecomposed portion of chlorate of potassa, and so converts it into perchlorate*.

Perchlorate of potassa may be formed, without risk of explosion, by heating the chlorate in nitric acid, 4 atoms of the chlorate yielding 1 of the perchlorate. (See p. 565.)

* Millon (*Ann. Ch. et Ph.*, 1843,) has suggested other views respecting the compounds of chlorine and oxygen, and the constitution of the chlorates. He describes 7 compounds, which he names as follows:--

1. Hypochlorous acid ClO
2. Chlorous acid ClO₃
3. Hypochloric acid ClO₄ = Cl₄O₁₆ = 3[ClO₃], ClO₇
4. Chloric acid ClO₅ = Cl₂O₁₀ = ClO₃, Cl₇
5. Chlorochloric acid Cl₃O₁₃ = 2[ClO₃] + ClO₇ (euchlorine of Davy).
6. Chloroperchloric acid Cl₃O₁₇ = ClO₃ + 2[ClO₇]
7. Perchloric acid..... ClO₇

Of these the hypochlorous, chlorous, and perchloric acids are considered as independent compounds: he represents his hypochloric acid as including 3 equivalents

Perchlorate of potassa does not change vegetable colors, nor is it altered by exposure to air. Its taste resembles that of chloride of potassium. It crystallizes in anhydrous rhombic prisms. It requires rather more than 65 parts of water at 60° for its solution: it is more soluble in boiling water; insoluble in alcohol. (SERULLAS, *Ann. Ch. et Ph.*) It is the difficult solubility of this salt which has suggested the occasional use of perchloric acid as a precipitant of potassa salts. It detonates slightly when rubbed with sulphur. When mixed with its own weight of sulphuric acid, and distilled at 280° , aqueous oxychloric acid passes over. It may be decomposed by exposure to a temperature of 412° ; oxygen is given off, equal to 0.45 *per cent.* of the weight of the salt, and chloride of potassium remains in the retort.

Gmelin states that when a saturated solution of chlorate of potassa is exposed to the decomposing agency of Voltaic electricity, transmitted by platinum poles, crystals of perchlorate of potassa are formed at the positive pole, whilst hydrogen is evolved at the negative.

The ultimate elements of this salt are

Oxygen	8	64	45.7
Chlorine	1	36	25.7
Potassium	1	40	28.6
	<hr/>		<hr/>		<hr/>
	1		140		100.0

Its proximate composition:

						Stadion.
Potassa	1	48	34.3 34.31
Perchloric acid	1	92	65.7 65.69
	<hr/>		<hr/>		<hr/>	<hr/>
Perchlorate of potassa	1		140		100.0	100.00

IODIDE OF POTASSIUM. KI. Iodine and potassium act upon each other very energetically, and often with explosion, evolving heat and light, and a crystalline compound is obtained, white and fusible. Potassium also burns when heated in the vapor of iodine. When hydriodic acid is saturated by potassa, and the solution carefully evaporated, anhydrous crystals of the iodide (or as it is sometimes called *hydriodate of potassa*) are obtained. The usual mode of procuring this compound consists in dissolving iodine in solution of potassa, till it begins to assume a brown color: on evaporating to dryness, and fusing the residuary salt at a red heat, iodide of potassium remains, generally mixed, however, with a little iodate: if a little charcoal be added previous to fusion, the decomposition is complete. (SCANLAN.) If, instead of fusing the products, the solution be carefully evaporated nearly to dryness, and alcohol poured upon it, the iodide is dissolved, and there remains a salt insoluble in alcohol, which is *iodate of potassa*, and which, at a red-heat, evolves oxygen, and becomes iodide of potassium. The action of iodine upon the alkali appears in all respects to correspond with that of chlorine, that is, 6KO , and 6I , produce 5KI , and KO, IO_5 , and then by the application

of chlorous, and 1 of perchloric acid; chloric acid as including 1 equivalent of chlorous and 1 of perchloric acid: chlorochloric acid as including 2 equivalents of chlorous, and 1 of perchloric acid. With the exception of the chloric and perchloric acids, Millon

represents the above compounds as volatile liquids yielding yellow and highly explosive vapors. He considers chlorate of potassa as $\text{KO}, \text{ClO}_3 + \text{KO}, \text{ClO}_7$, and that in its decomposition by heat, the former salt is that from which the first oxygen is evolved.

of heat KO, IO_5 , becomes KI , and O_6 are driven off. "A certain loss may occur in this process if the heat applied be too high; and if the temperature be not high enough, iodate of potassa may remain undecomposed; this last effect being advantageous to the manufacturer by increasing the quantity of the product, is more liable to occur, and may be detected by means of tartaric acid, as ingeniously proposed by Scanlan: this acid is without action on pure iodide of potassium further than to liberate hydriodic acid, which remains for a certain time unaltered; but if a trace of iodate of potassa be present, the iodic acid which it sets free immediately reacts on the hydriodic acid, water being formed and iodine liberated, which may be recognized by means of starch." (KANE, *El. Ch.*, 692.) Dr. Turner prepared iodide of potassium as follows: add as much iodine to a hot solution of caustic potassa as it will dissolve, and pass sulphuretted hydrogen through the mixture till it becomes colorless; expel any excess of sulphuretted hydrogen by heat, filter, neutralize with potassa, and crystallize: in this case the iodic acid is decomposed by the sulphuretted hydrogen, and nothing but iodide of potassium remains in solution.

Iodide of potassium is also prepared by decomposing a solution of iodide of zinc by carbonate of potassa, (when $\text{ZnI} + \text{KO}, \text{CO}_2$ become KI and $\text{ZnO} + \text{CO}_2$), and filtering off and evaporating the resulting solution of the iodide, which, however, is apt to retain iodide of zinc. The Pharmacopœia directs the decomposition of a solution of iodide of iron by carbonate of potassa, when $\text{FeI} + \text{KO}, \text{CO}_2$ become KI , and $\text{FeO} + \text{CO}_2$; but in this case all traces of iron are difficultly got rid of.

Iodide of potassium forms cubic and prismatic crystals: they are anhydrous, and slightly deliquescent in damp air. According to Gay Lussac, 100 parts of water at 65° dissolve 143 of this salt, and a considerable depression of temperature is produced during the solution; it is sparingly soluble in absolute alcohol, but much more so in alcohol, sp. gr. $\cdot 850$. It is used in medicine, and as it occurs in commerce is frequently mixed with chloride of potassium and sodium, and with sulphate and carbonate of potassa. It should be purchased in crystals, which ought not to be very deliquescent, and should perfectly dissolve in six or eight parts of alcohol, sp. gr. $\cdot 836$. They generally redden turmeric from the presence of a little adhering carbonate of potassa. According to R. Phillips, jun. (*Pharm. Journ.*, iv. 59,) the usual impurities in the iodide are chloride of potassium and sodium, iodate of potassa, and water. To detect chlorine, the iodide may be decomposed by nitrate of silver, and the washed precipitate digested in strong solution of ammonia; if the filtered solution acidified by nitric acid give a white precipitate, it is chloride of silver. To detect iodate of potassa, dissolve in cold water, acidulate with tartaric acid, and add solution of starch; if no dark color is produced, no iodate is present.

Iodide of potassium consists of

						Gay Lussac.
Potassium	1	40	24 23·8
Iodine	1	126	76 76·2
<hr/>						<hr/>
Iodide of potassium	1		166		100	100·0

The aqueous solution of iodide of potassium dissolves a considerable portion of iodine; this solution, under the name of *ioduretted iodide of*

potassium, is sometimes used in medicine: it is of a deep brown color. According to Baup a saturated solution of iodide of potassium will dissolve two equivalents of iodine, one of which falls on diluting the solution; but according to Labouré, this and similar combinations of iodine with the soluble iodides are not definite, and the quantity of iodine taken up varies with the strength of the solution. When shaken with ether, the whole of the free iodine is abstracted and floats upon the colorless solution of the iodide. (*Ch. Gaz.*, Jan. 1844.)

Iodide of potassium is decomposed by chlorine, and even when largely diluted a very minute quantity of chlorine discolors the solution: sulphuric and nitric acids also discolor it. Bichloride of platinum reddens a solution containing only a 12000th of the iodide; and protonitrate of mercury produces a yellow cloud where only a 60000th is present. (DUBLANC, *Journ. Chim. Med.*, ii. 120.) Paper which has been bleached by chlorine is generally discolored by iodide of potassium; and if characters be written or figures drawn with solution of iodide of potassium, they are rendered visible in the manner of sympathetic ink, by the slightest breath of chlorine.

IODITE OF POTASSA. When equivalents of iodine and of common caustic potassa are dissolved in water, and evaporated to dryness, without heating so far as to expel oxygen, the residue, being redissolved in water, and evaporated, yields large crystals, differing in form from the iodide or iodate: they are resolved by alcohol into iodide of potassium, which dissolves, and leaves iodate of potassa. (REIMAN.)

IODATE OF POTASSA. KO, IO_5 , or K, IO_6 , is, as above stated, one of the products of the action of iodine on solution of potassa, and after evaporation the iodide of potassium may be separated from the iodate by digestion in alcohol, sp. gr. 810, which leaves the latter salt undissolved. Iodate of potassa is also formed by gradually adding 3 parts of chlorate of potassa to 2 of fused iodide of potassium; a mixture of chloride of potassium and iodate of potassa results, which dissolved in hot water, deposits the latter salt on cooling: it may be purified by dissolving it in water, and precipitating by alcohol. (HENRY, *Journ. de Pharm.*, xviii. 345.)

Iodate of potassa requires about 14 parts of water at 60° for its solution: or, according to Gay Lussac, it dissolves in 13 parts of water at the temperature of 55° : it is perfectly insoluble in absolute alcohol; it is more soluble in a solution of iodide of potassium than in pure water. Its crystals are small cubes, permanent in the air; at a red heat, it gives out between 22 and 23 *per cent.* of oxygen, and is converted into iodide of potassium, no periodate being intermediately formed: it deflagrates upon red-hot charcoal with a purple flame. Its aqueous solution is decomposed by sulphuretted hydrogen, and by sulphurous and arsenious acids: with strong hydrochloric acid it yields chloriodide of chloride of potassium, chlorine, and water. ($\text{KO}, \text{IO}_5 + 6\text{HCl} = \text{KCl}, \text{ICl}_5 + 2\text{Cl} + 6\text{HO}.$) **FILHOL.** Its solution in excess of hot nitric acid deposits crystals of iodic acid on cooling, and nitrate of potassa remains dissolved: when evaporated it leaves 1 atom of nitre, and 1 of biniodate of potassa: at a higher temperature the nitric acid goes off as oxygen and nitrous acid, and iodate of potassa remains. (PENNY.)

Iodate of potassa consists of

Potassa	1	48	22·54
Iodic acid.....	1	166	77·46
<hr/>					
Iodate of potassa	1		214		100·00

Serullas has described a *biniodate* and a *teriodate* of potassa. (*Ann. Ch. et Ph.*, xliii. 113.) The biniodate is obtained by adding an additional equivalent of iodic acid to a solution of the neutral iodate saturated at a high temperature: it forms prismatic crystals with dihedral summits, which retain an equivalent of water, but which, according to Graham, may be rendered anhydrous by heat: it is soluble in 75 parts of water at 60°. The *teriodate* is formed when a strong acid is added to a hot saturated solution of the neutral iodate, and allowing it to cool slowly: it forms rhombohedral crystals soluble in 25 parts of water. According to Serullas the biniodate of potassa has a great tendency to form double salts; one of these, with *chloride of potassium*, is obtained in crystals, when a little hydrochloric acid is added to a solution of iodate of potassa and the mixture subjected to spontaneous evaporation: it contains 1 atom of the biniodate with 1 of chloride; it cannot be formed by the direct union of its component salts, and is decomposed by water. Another double salt of biniodate with *bisulphate of potassa* is obtained from the mother-liquor which remains when teriodate of potassa is prepared by means of sulphuric acid; it forms crystals which are decomposed by water, and, like the preceding, cannot be formed directly.

BROMIDE OF POTASSIUM. K,Br. Potassium and bromine act intensely upon each other, evolving heat and light, and producing explosion. When bromine is dropped into solution of potassa, the mixture evaporated, and the residue heated to redness, *bromide of potassium* is also obtained. Its sp. gr. is 2·4: it is white, fusible, and crystallizes in cubes, easily soluble in water, and slightly so in alcohol. It consists of

						Liebig.	Balard.
Potassium	1	40	33·9	32·58
Bromine	1	78	66·1	67·42
<hr/>						<hr/>	<hr/>
Bromide of potassium....	1		118		100·0		100·00

It is prepared for medical use, either by the above process, or by decomposing bromide of zinc or bromide of iron, by carbonate of potassa; it should be purchased in crystals, as it is otherwise apt to be impure. It yields the red fumes of bromine when acted on by sulphuric acid. According to Kane, the commercial article is frequently adulterated with chloride of potassium, the presence of which may be detected as follows: "Dissolve 100 grains of the salt in 4 ounces of water, and decompose it by an excess of nitrate of silver, collect the precipitate, wash, and carefully dry it in a capsule till it ceases to lose weight, then weigh it. If it were perfectly pure the bromide of silver should weigh 158·8 grains, but the presence of chloride of potassium would have the effect (from the smaller equivalent of chlorine,) of increasing the weight; therefore, if the precipitate when quite dry weighs more than 158·8 grains, the sample is impure, and the quantity of chloride present may be calculated from the overplus weight, for 100 grains of pure chloride of potassium should give 192·6 of precipitate. Thus, if there were 10 *per cent.* of impurity the

precipitate would weigh 162 grains; if 20 *per cent.* it would weigh 165·4 grains. Thus, the precipitate increases in weight about 3·3 for each 10 *per cent.* of chloride of potassium present."

The method employed by Rose for detecting minute quantities of the chlorides in the bromides, is the following (PEREIRA, *Elem. Mat. Med.*): If pure bromide of potassium mixed with excess of bichromate of potassa be distilled with concentrated sulphuric acid in a tubulated retort, to which is adapted a receiver containing excess of solution of caustic ammonia, pure bromine distils over, and the ammoniacal liquor remains perfectly colorless. But if the bromide contained a chloride, both bromine and the chromate of chloride of chromium distil over, and the ammoniacal liquor becomes yellow: chromic acid may be detected in the solution by the usual tests. (*Journal de Pharmacie*, xxiii. 489.)

When ethereal solution of bromine is agitated with liquid potassa, the yellow color disappears, and bromate of potassa and bromide of potassium are the results. The action, therefore, of bromine is here analogous to that of chlorine and iodine. Chlorine expels bromine from its combination with potassium, at a red heat; but bromine expels iodine.

BROMATE OF POTASSA. KO, BrO_5 , or K, BrO_6 , separates in the form of a crystalline powder, when bromine and solution of potassa are mixed in sufficient quantities. By slow evaporation it yields four and six-sided tabular crystals and cubes, with truncated angles. It scintillates on a hot coal, like nitre, and evolving oxygen becomes bromide of potassium. It is very slightly soluble in alcohol: soluble in 15 parts of water at 60° : mixed with sulphur it detonates by a blow. Its solution occasions a white precipitate in nitrate of silver. (BALARD, *Quarterly Jour.*, xxii. 389.)

FLUORIDE OF POTASSIUM. KF . When hydrofluoric acid is saturated with potassa, and evaporated to dryness, a deliquescent and difficultly crystallizable compound is obtained, which must be regarded as a *fluoride of potassium*. It probably consists of

Potassium	1	40	67·80
Fluorine	1	19	32·20
<hr/>					
Fluoride of potassium	1		59		100·00

This fluoride bears an intense heat without change. Its solution acts upon glass. It is decomposed by chlorine, and by sulphuric acid, which immediately expels hydrofluoric acid.

Berzelius has described an apparently peculiar compound, obtained by dissolving the above fluoride in hydrofluoric acid, and evaporating to dryness in a platinum vessel: it is crystallizable, readily soluble in water, and when heated to incipient redness is decomposed, hydrofluoric acid being evolved, and fluoride of potassium remaining. It appears to consist of

						Berzelius.
Fluoride of potassium	1	59	75·95 74·9
Hydrofluoric acid	1	20	24·05 25·1
<hr/>						
	1		79		100·00	100·0

POTASSIUM AND HYDROGEN. When potassium is heated to incipient redness in hydrogen, it absorbs a portion of the gas, and produces a grey infusible *hydruret*, destitute of lustre, and burning when heated in air or oxygen. At a high red heat, it evolves hydrogen; and the same change takes place in the contact of mercury. (JACQUELAIN, *Ann. Ch. et Ph.*, LXXIV. 203.)

When hydrogen and potassium are passed together through a white-hot tube, a spontaneously inflammable *potassiuretted hydrogen gas* is formed. Potassiuretted hydrogen is also produced when potassium is thrown upon water, and is the cause of the red flame and white fumes produced during its combustion under such circumstances. Both these compounds are usually formed during the operation for obtaining potassium by the gun-barrel. (GAY LUSSAC and THIENARD.) But when potassiuretted hydrogen cools it deposits the whole of the potassium, so that it is probably a mere mixture of hydrogen and potassium vapor.

HYPONITRITE OF POTASSA. KO, NO_3 . When basic hyponitrite of lead is decomposed by carbonate of potassa, or when nitre is fused in a platinum or iron crucible till the evolution of oxygen begins to decrease, a hyponitrite is formed: the residuary salt is dissolved, and yields at first crystals of nitre, and afterwards of hyponitrite. This salt is colorless, neutral, and slightly deliquescent: it may be obtained perfectly pure by decomposing hyponitrite of silver by chloride of potassium: it has a great tendency to form double salts: as it gives off nitric oxide when acted upon by a stronger acid it was long regarded as a compound of nitric oxide and potassa, but Mitscherlich has shown that no such compound is as yet known, and that when nitre is heated oxygen first goes off, and hyponitrite of potassa is formed, and afterwards hyponitrous acid escapes, and potassa remains. (BERZELIUS.)

NITRATE OF POTASSA. NITRE. SALTPETRE. KO, NO_5 , or K, NO_6 . This salt is an abundant natural product, and is principally brought to this country from the East Indies, where it is produced by lixiviation from certain soils; but the mode or cause of its formation is not understood: it is probably connected with the oxidizement of ammonia. The greater part of the rough nitre imported from the East Indies is in broken crystals of a brown color, and more or less deliquescent; exclusive of other impurities, it often contains a considerable portion of common salt, which, re-acting upon the nitre sometimes induces the production of nitrate of soda and chloride of potassium: it also usually contains sulphate of lime, and often traces of organic matter.

In Germany and France it is artificially produced in what are termed nitre-beds. Thenard (*Traité de Chimie Élémentaire*) has described the French process at length. (See also DUMAS, *Chim. app. aux Arts*, ii. Kuhlman endeavoured to cause oxygen and hydrogen to combine in contact with spongy platinum, but without success, *Mém. Acad. Sciences de Lille*, 1838; see also LIEBIG'S *Ann.*, xxix. 272.) It consists in lixiviating old plaster rubbish, which, when rich in nitre, affords about five *per cent.* Refuse animal and vegetable matter, which has putrified in contact with calcareous soils, produces nitrate of lime, which affords nitre by mixture with carbonate of potassa. In the same way it is

abundantly produced in some parts of Spain. Exudations, containing saltpetre, are not uncommon upon new walls, where it appears to arise from the decomposition of animal matter contained in the mortar. It was long ago shown by Glauber, that a vault plastered over with a mixture of lime, wood-ashes, and cows' dung, soon becomes covered with efflorescent nitre, and that, after some months, the materials yield, on lixiviation, a considerable proportion of that salt.

The loss which rough nitre sustains in refining, is technically termed the *refraction*, and can only be ascertained by analysis, which frequently is somewhat intricate: it is, moreover, not easy to get a fair sample of a cargo. The samples which the merchants and brokers select for analysis, generally consist of portions drawn from each bag and afterwards mixed together, and if carelessly or unfairly taken, or exposed so as to become more moist or more dry than the bulk, the report of the analyst is often unsatisfactory. He should work upon not less than 20 to 30 lbs. of such sample, which should be ground or triturated so as to produce a properly uniform mixture of the whole, for it often includes lumps of pure nitre or of other salts; from 100 to 1000 grains of this mixture is then taken for analysis. The moisture is determined by the loss occasioned by careful drying on the sand-bath; it is then dissolved in water and tested, so as to acquire some general notion of the impurities; and, by means of nitrate of silver, nitrate of baryta, and oxalate of ammonia, the proportion of chlorine, sulphuric acid, and lime, may be determined: the lime is generally in the state of sulphate, and more or less sulphate of potassa is also usually present; the chlorine is chiefly derived from the chlorides of potassium and sodium. Another portion of the sample should be dissolved in about thrice its weight of boiling water, and filtered, by which any sand or other insoluble impurities are collected; the salt should then be crystallized in the usual way, during which the appearances and forms of the successive deposits will indicate, to the experienced eye, the nature of the foreign salts present; among which nitrate of soda, sulphate of potassa, sulphate and nitrate of lime, and chloride of sodium and potassium, with traces of chloride of calcium, and sometimes of a peculiar organic matter, are frequently found. It will be obvious that the accurate quantitative analysis of such a mixture of salts is not a very easy problem, and yet the separation of nitrate of soda from nitrate of potassa, and of chloride of potassium from chloride of sodium, are essential steps, as the value of the sample is affected by their relative proportions: for nitrate of soda, to say nothing of its unfitness for the manufacture of gunpowder, is cheaper than nitrate of potassa; and chloride of sodium is of no value, whereas chloride of potassium is purchased by the alum-makers; so that a sample of nitre, containing the latter salt, is in this respect worth more than where it only contains common salt. But inasmuch as the equivalent of chloride of sodium is only 60, and that of chloride of potassium 76, it is obvious that if the whole of the chlorine, as indicated by the weight of the chloride of silver, be considered as in combination with sodium (part of the sample consisting of chloride of potassium), the refraction will be estimated below the mark. Hence the necessity of ascertaining the relative proportions of both chlorides, which is best effected by converting them into sulphates, and separating them by crystallization.

A rough method of determining the value of a sample of nitre, and which, in some cases, especially where common salt is the chief impurity, admits of considerable accuracy, consists in putting a pound of the salt in powder into a basin, and pouring upon it a pint of a saturated aqueous solution of pure nitre; this mixture is well stirred for 15 or 20 minutes, then left at rest, and when the salt is deposited, the liquor is poured off and filtered: half a pint of the saturated solution of pure nitre is then again poured upon the remaining salt, stirred as before, and then the whole contents of the basin are carefully transferred into the filter. In some cases where the quantity of common salt is excessive (exceeding 66 *per cent.*) the washing must be repeated a third time, but this is rarely necessary. When the dripping of the filter has ceased, it is carefully removed with its contents, from the funnel, and placed upon a few sheets of coarse filtering paper lying upon a chalk table or other absorptive substance, the saltpetre being carefully spread out so that the moisture may be absorbed. When it is dry enough to admit of removal, it must be carefully transferred into a basin placed upon a sand-bath, and the drying completed till it no longer adheres to the rod or ivory knife with which it is stirred; it is then weighed, and the loss of weight, (as compared with the sample,) gives the impurities; but from this, 2 *per cent.* should be deducted for the nitre deposited by the saturated solution whilst taking up the common salt. When the common process for refining nitre is conducted as follows, it may be made subservient to the more accurate analysis.

Purification of Nitre. A given quantity of the rough salt (say 7 lbs.) is accurately weighed, and then dissolved by heat in 3 or 4 parts of water; when boiling, the scum is removed until no more rises, and then the solution is allowed to settle for ten minutes or longer. In this way nearly all the dirt falls down, and the clear solution, being poured off, is passed through a filter of tow into a pan, and set aside to crystallize; the dirt left behind is added to the scum, and both being diluted, are filtered through paper, and the clear solution preserved. Next day the crystals formed in the pan are separated and put into funnels to drain, and the mother-liquor with the filtered solution from the scum, &c. are further evaporated, and again left to crystallize. On the second evaporation, impurities generally separate from the solution; these are sometimes oxide of iron, or sulphate of lime, but most frequently chloride of sodium and of potassium, sulphate of potassa, and nitrate of soda. The two first are easily separated by filtration; the chlorides are best separated by evaporating the solution considerably, until much salt has been deposited, and then pouring the whole upon a filter of tow; the common salt, with more or less of the others, will remain on it, and should be washed with a little water to separate the nitre, which water should be added to the liquor, and the whole then brought to the crystallizing point. When cold, the crystals deposited by this solution are to be separated as before, until the mother-liquor is divided into other salts and nitre. It frequently happens that the crystals from the two or three last evaporations are colored or contaminated by the adhesion of common salt, sulphate of lime, &c.; in this case, they should be re-dissolved and re-crystallized with the same precautions as before. Care should be taken in drying the crystals, especially when large, that no water remains in their interstices,

which is often the case to a considerable extent; and not unfrequently the interstitial water retains foreign salts, so that, in purifying nitre upon the large scale, it is often advantageous to stir it whilst crystallizing, that the crystals may be small and broken, and then the adhering impurities may be better washed out by cold water. When pure, the solution of nitre is not rendered turbid either by nitrate of silver or nitrate of baryta.

Nitre crystallizes in six-sided prisms, usually terminated by dihedral summits. Its specific gravity is 1.933 to 2.10. Its primitive form is a right rhombic prism. (LEVY, *Quarterly Journal*, xv. 284.) A solution of nitre crystallized at a very low temperature (15°), or to which alcohol has been added, deposits mixed prismatic and rhombohedral crystals. When a drop of solution of nitre evaporates upon a glass plate, the crystals viewed under the microscope are partly rhomboids and partly prisms: the rhomboids afterwards disappear and redissolve, especially if touched. (FRANKENSTEIN, *Poggend.*, xl. 447.) The crystals are large and smooth when obtained from a great mass of solution, but irregular and striated when formed in smaller quantities. The large crystals, when handled, generally crack transversely; so that it is difficult to preserve them entire. (See fig. 11.) They are not altered by exposure to air. La Grange states that 1 part of nitre dissolves in between 3 and 4 of water at 60° , and in half its weight at 212° . Gay Lussac has shown that the solubility of nitre varies extremely with temperature: at 32° , 100 parts of water dissolve 13.2 of the salt; at 77° , the salt dissolved by 100 of water is 38 parts; at 132° , it amounts to 97 parts; at 176° , to 169 parts; at 210° , to 236 parts; and at 212° , to 246 parts. According to Dr. Ure, the temperature of a saturated solution of nitre, boiling hot, is 340° , and the relation of the salt to its solvent is in weight as 3 to 1. Upon the same authority, water at 60° dissolves one-fourth its weight of nitre; or, more exactly, this saturated solution contains 21 *per cent.* of salt; its specific gravity is 1.1415; and 100 parts in volume of the two constituents occupy now 97.91 parts. (*Jour. Roy. Inst.*, i. 121.) Berzelius observes, that the solubility of nitre is apparently increased by the presence of common salt, but that this arises from their mutual reaction, producing nitrate of soda and chloride of potassium. Yet, during crystallization, common salt and nitre separate distinctly from each other. During the solution of 1 part of powdered nitre in 5 of water, the temperature sinks from 50° to 35° . Its use in cooling mixtures has already been noticed. (p. 69.) It is insoluble in pure alcohol. The crystals of nitre, though the salt is anhydrous, generally contain interstitial water; so that they appear moist when powdered, and lose weight on drying. The taste of nitre is cooling and peculiar: it is used in medicine in small doses, as a diuretic and sedative; in doses of from half an ounce to an ounce it is poisonous, exciting spasms, vomiting, bloody stools, convulsions, and often proving fatal. In such cases viscid mucilaginous drinks with opium and cordials are the most effective restoratives. This salt consists of

						Wollaston.	Wenzel.		
Potassa	1	48	47.1	46.668	48
Nitric acid	1	54	52.9	53.332	52
<hr/>									
Nitrate of potassa.....	1		102		100.0		100.000		100

Its ultimate components are*,

Oxygen	6	48	47·06
Nitrogen.....	1	14	13·72
Potassium	1	40	39·22
<hr/>					
Nitrate of potassa	1		102		100·00

At a temperature of about 600°, nitre fuses without undergoing change of composition, and congeals, on cooling, into a white striated mass. Sometimes it is cast into small balls or cakes, called *sal prunella*, a name said to be derived from the circumstance of its having been occasionally stained of a plum-color. At a red-heat, nitre is slowly decomposed; and if highly heated in an earthen retort or gun-barrel, it affords abundance of oxygen gas, one pound yielding about 12,000 cubic inches, of sufficient purity for many common experiments in which that gas is used; it is of course mixed with a portion of nitrogen. In this decomposition the nitre is first converted into *hyponitrite of potassa*, which is somewhat deliquescent; and potassa is the final result.

Nitre is rapidly decomposed by charcoal at a red heat; and the results are carbonic oxide and acid, nitrogen, and carbonate of potassa, formerly called *nitrum fixum*, and *white flux*. The old chemists used to perform this detonation in retorts connected with capacious receivers, which were generally blown to pieces; sometimes they succeeded in obtaining a little acidulated water, which they called *clyssus of nitre*, and attributed to it wonderful medical virtues. These mixtures of nitre and charcoal form the basis of a variety of compositions used for fireworks, the rapidity of the combustion being modified by the relative proportion of the charcoal. When phosphorus is thrown upon nitre, and inflamed, a vivid combustion ensues, and a phosphate of potassa is formed. Sulphur sprinkled upon hot nitre burns, and produces a mixture of sulphate and sulphite of potassa, formerly employed in medicine, under the name of *Glaser's polychrest salt*. The combustion of a mixture of sulphur with a small quantity of nitre has already been described as a source of sulphuric acid. (p. 387.) When a mixture of 2 parts of nitre and 1 of hydrochlorate of ammonia are heated to redness, chloride of potassium, water, chlorine, hydrochloric acid, and a little nitrous acid, are the results, and nitrogen gas is copiously evolved. (SOUBEIRAN, *Journ. de Pharm.*, 1827, p. 321.) Most of the metals, when in filings or powder, detonate and burn when thrown on red-hot nitre; some of the more inflammable metals produce in this way a considerable explosion.

A mixture of 3 parts of nitre, 2 of dry carbonate of potassa, and 1 of sulphur, forms *fulminating powder*. If a little of this compound be heated upon a metallic plate to about 330°, it blackens, fuses, and explodes with much violence, in consequence of the rapid action of the sulphur upon the nitre, and the sudden evolution of nitrogen and carbonic acid, the residue being chiefly sulphate of potassa. $3[\text{KO}, \text{NO}_5] + 2[\text{KO}, \text{CO}_2] + 5\text{S} = 5[\text{KO}, \text{SO}_3] + 3\text{N} + 2\text{CO}_2$. A mixture of 3 parts of nitre, 1 of sulphur, and 1 of fine sawdust, constitutes *Baumé's flux*: a little of it

* In the electrolysis of a solution of nitre, the results indicate that an atom of potassium travels to the negative electrode, and an atom of nitrogen and six atoms of oxygen to the positive electrode; hence the electrolytic formula of nitre is K, NO_6 , or an *oxynitron of potassium*. (DANIELL, *Phil. Trans.*, 1839, p. 109, and 1840, p. 223.)

inflamed in a walnut-shell fuses a small silver or copper coin. The lucifer matches which inflame by friction are tipped with a mixture of phosphorus and nitre, with the addition generally of red-lead or oxide of manganese and gum arabic: some of them also contain sulphur and chlorate of potassa. (BÖTGER, *Ann. de Pharm.*, xxvii. 113.)

The action of sulphuric acid on nitre has been described above (p. 337), and will be again adverted to under *sulphate of potassa*. When nitre and hydrochloric acid are heated together, chlorine and nitrous acid are evolved, and on evaporation to dryness, chloride of potassium remains. Penny proposes this decomposition as the basis of a method of ascertaining the quantity of nitrate of potassa in crude saltpetre. (*Phil. Trans.*, 1839, p. 13.)

GUNPOWDER consists of a very intimate mixture of nitre, sulphur, and charcoal, the proportions varying according to the uses made of it, as follow :

	Common gunpowder.	Shooting powder.	Shooting powder.	Miners' powder.
Saltpetre	75·0	78	76	65
Charcoal.....	12·5	12	15	15
Sulphur	12·5	10	9	20

The following is a table of the composition of gunpowder of several countries:

	Nitre.	Charcoal.	Sulphur.
Waltham Abbey mills	75	15	10
France, national establishment	75	12·5	12·5
——— for sportsmen	78	12	10
——— for mining.....	65	15	20
United States of America	75	12·5	12·5
Prussia.....	75	12·5	12·5
Russia	73·78	13·59	12·63
Austria	76	11·5	12·5
Spain	76·47	10·78	12·75
Switzerland (round powder)	76	14	10
Chinese	75	14·4	9·9

The ingredients are *perfectly* mixed, moistened, beaten into a cake, which is afterwards broken up, granulated, dried, at 140° to 150°, and for the finest powder polished by attrition. The violence of the explosion of gunpowder depends upon the sudden production of gaseous matter, and of intense heat, resulting from the action of the combustibles upon the nitre. Carbonic oxide, carbonic acid, nitrogen, and sulphurous acid, are the principal gaseous results; and the solid residue consists of carbonate and sulphate of potassa, sulphuret of potassium, and charcoal. (CRUICKSHANKS, *Nicholson's Journal*, iv. See also the same *Journal*, xiii. 277.)

If we theoretically inquire how the maximum gaseous volume is to be produced from the chemical reaction of the elements of gunpowder, we shall find it to be by the generation of carbonic oxide and sulphurous acid, with the disengagement of nitrogen. This will lead to the following proportions of their constituents. (URE, *Jour. Roy. Inst.*, vol. i. p. 135.)

		Per cent.
1 equivalent of nitre	102	75·00
1 „ sulphur.....	16	11·77
3 „ charcoal	18	13·23
	136	100·00

The nitre yields 5 proportionals of oxygen, of which 3 combining with 3 of charcoal will furnish 3 of carbonic oxide gas, while the remaining 2 will convert the 1 of sulphur into sulphurous acid gas: the single proportional of nitrogen is, therefore, in this view disengaged alone. The gaseous volume, on this supposition, evolved from 130 grains of gunpowder, equivalent in bulk to 75.5 grains of water, or to three-tenths of a cubic inch, will be at the atmospheric temperature as follows:

	Grains.	Cubic inches.
Carbonic oxide.....	42	141.6
Sulphurous acid	32	47.2
Nitrogen	14	47.4
		<hr/> 236.2

Being an expansion of 1 volume into 787.3. But as the temperature of the gases at the instant of their combustive formation must be incandescent, this volume may be safely estimated at three times the above amount, or considerably above two thousand times the bulk of the solid.

But this theoretical account of the gases developed does not exactly accord with the experimental products usually assigned, especially as relates to the evolution of carbonic acid, and to the residuary sulphuret of potassium; with these, the following view of the results of the deflagration given by Graham, is more consistent.

Before combustion.		After combustion.	
3	equivalents of carbon.....	} 3 carbonic acid	
1	„ of nitre { 6 oxygen		1 nitrogen
1	„ of sulphur { 1 nitrogen		
			1 sulphuret of potassium

Carburetted and sulphuretted hydrogen, and vapor of water, often mentioned among the products of the combustion of gunpowder, are found in very minute quantities only, for good gunpowder does not contain more than 1 *per cent.* of water, which can be the only source of hydrogenated compounds. The principal use of the sulphur is to increase the combustibility of the powder in consequence of the comparatively low temperature at which it takes fire, but the larger the proportion of sulphur the less forcible will be the explosion of the powder: thus, when it contains 12 of charcoal and 12 of sulphur in 100, it does not throw a proof-shell so far as that containing 19 of charcoal and 9 of sulphur. But the former powder keeps better than the latter, so that for the supply of remote colonies and humid climates, it perhaps justifies a slight sacrifice of strength, which may be compensated by a larger charge. The granulation of gunpowder increases its explosive force and rapidity of combustion, the charge being sufficiently porous to admit of the flame penetrating it so as to kindle every grain nearly at the same instant; in mass, in a compressed state, as before it is broken up for granulation, its combustion is much more gradual. But although the combustion of gunpowder is very rapid, it is by no means instantaneous, for in that case scarcely anything would resist its power, and its explosion would more resemble that of fulminating mercury, or silver, or the chloride or iodide of nitrogen, and like those substances it would burst the gun without propelling the ball. (For the details of the manufacture of gunpowder, see COLEMAN, *Phil. Mag.*, ix.; AIKIN'S *Dictionary of Chemistry* (article,

GUNPOWDER); URE's *Dictionary of Arts and Manufactures*; and DUMAS, *Chimie app. aux Arts*.)

The strength and goodness of gunpowder is most accurately determined by measuring its actual projectile force by the *épreuve*, which is a small strong barrel in which a given quantity of it is fired, and the force of expansion measured by the action exerted on a strong spring or a great weight. Another method is, to fire a heavy ball from a short mortar, with a given weight of the powder, and to find the range of projection. The *épreuve* formerly used in France, was a mortar seven inches (French) in calibre, which, with three ounces of powder, should throw a copper globe of 60 lbs. weight to the distance of 300 feet. Gunpowder is sometimes tried by placing two heaps of about sixty grains each upon clean writing-paper, three or four inches asunder, and firing one of them by a red-hot wire: if the flame ascends quickly with a good report, sending up a ring of white smoke, leaving the paper free from white specks and not burnt into holes, and if no sparks fly off from it so as to set fire to the contiguous heap, the powder is very good; if otherwise, the ingredients are badly mixed or impure. It appears from Count Rumford's experiments on the force of gunpowder (*Phil. Trans.*, LXXXVII. 254), that 28 grains, confined in a cylindrical space which it just filled, tore asunder a piece of iron which would have resisted a strain of 400,000 lbs. (See also a report on M. PIOBERT'S *Memoir on Gunpowder*; *Ann. Ch. et Ph.*, LXII. 250.)

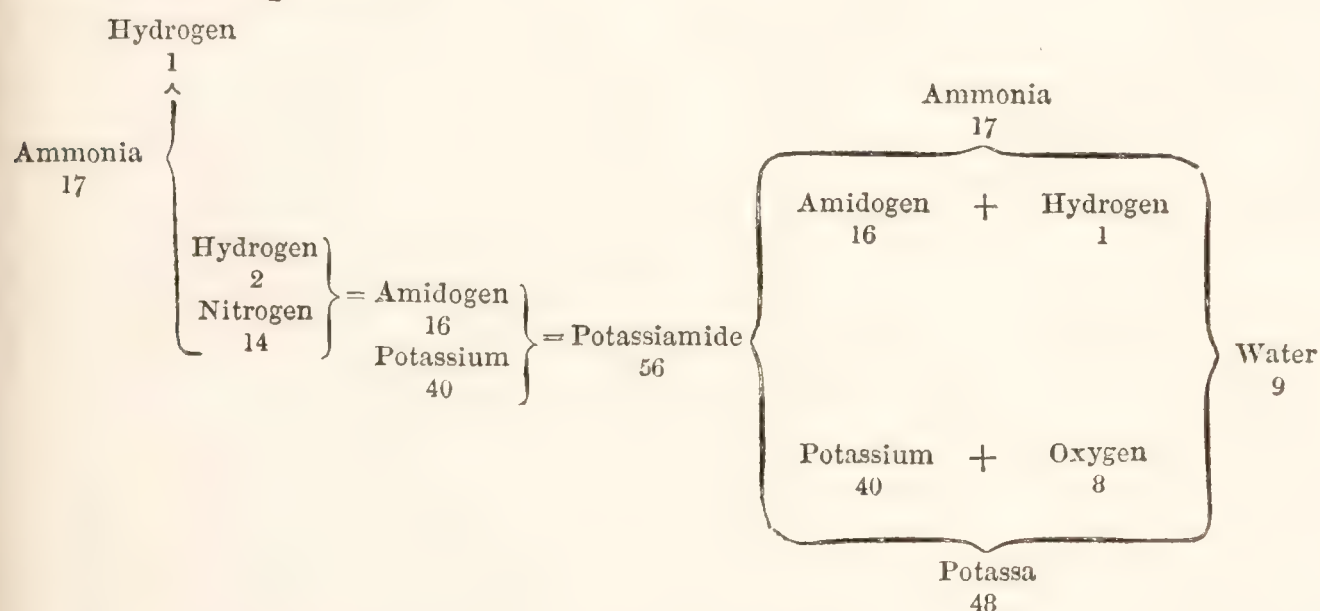
Gunpowder may, it is said, be inflamed by a violent blow; and if mixed with powdered glass, or any other harder substance, and struck with a heavy hammer upon an anvil, it almost always explodes. It readily burns under water, and by using a slowly burning powder, such as squibs are filled with, inflamed in a tube of copper, the gaseous products may be collected over water in the pneumatic trough. The portfires used by the artillery also answer very well for this experiment.

Analysis of Gunpowder. To analyze this compound, boil it with four parts of water, edulcorate the residue, dry it at 212° , and weigh; the loss indicates the nitre. The dry residue, composed of charcoal and sulphur, may be decomposed by spreading it upon an earthen plate, and burning off the sulphur at the lowest possible heat; the charcoal will remain, still however retaining a little sulphur. A more accurate process consists in introducing the powder into a small retort furnished with a stop-cock, exhausted, and filled with chlorine; heat applied volatilizes the chloride of sulphur and leaves the charcoal and nitre; which residue may be washed, dried, and the remaining charcoal weighed. Another mode of analyzing gunpowder consists in separating the nitre by water, evaporating to dryness, and fusing the salt. To obtain the sulphur, 5 grains of the powder, 5 of carbonate of potassa, 5 of nitre, and 20 of pure common salt, are to be intimately mixed, and placed on the fire in a platinum vessel; the sulphur is slowly acidified, and when the mass becomes white it is dissolved in water, saturated with nitric or hydrochloric acid, and solution of chloride of barium added, so long as it occasions a precipitate; the sulphate of baryta thrown down is then collected, washed, and ignited, and its weight indicates the quantity of sulphur contained in the gunpowder by the usual computation. (GAY LUSSAC, *Ann. Ch. et Ph.*, xvi. 437.) Sometimes after the separation of the nitre by water, the resi-

duary sulphur and charcoal are dried, and the relative proportion of the latter determined by ignition with oxide of copper, as in organic analyses. Bolley proposes to separate the sulphur from the charcoal by boiling in a solution of sulphite of soda, using 20 parts of the sulphite to 1 of the mixture of charcoal and sulphur. The sulphur might probably be effectually abstracted from gunpowder by the action of sulphuret of carbon.

ACTION OF POTASSIUM ON AMMONIA. POTASSIAMIDE. The action of potassium on gaseous ammonia was first examined by Gay Lussac and Thenard, and by Sir H. Davy. When potassium is heated in ammonia, hydrogen is evolved, and a fusible olive-colored substance is obtained, of a crystalline fracture, translucent at the edges, heavier than water, and a non-conductor of electricity. It fuses at a little above 212° . It burns in oxygen, producing hydrated potassa and nitrogen: exposed to air, it slowly deliquesces, and evolves ammonia: water rapidly acts upon it, producing potassa and ammonia. The volume of hydrogen evolved by this action of potassium on ammonia is the same as that which it would have evolved from water, so that when 1 atom of potassium acts on 1 of ammonia, 1 of hydrogen is evolved, and the remaining elements of the ammonia (namely 1 atom of nitrogen and 2 of hydrogen) combine with the potassium; now 1 of nitrogen and 2 of hydrogen constitute *amidogen*, (see p. 358;) hence this resulting compound has been termed *potassiamide*, its formula being K, NH_2 .

The following diagram, to which the equivalent numbers are attached, shows that ammonia, acted upon by potassium, loses one equivalent of hydrogen, and forms potassiamide; and that potassiamide and water yield ammonia and potassa:



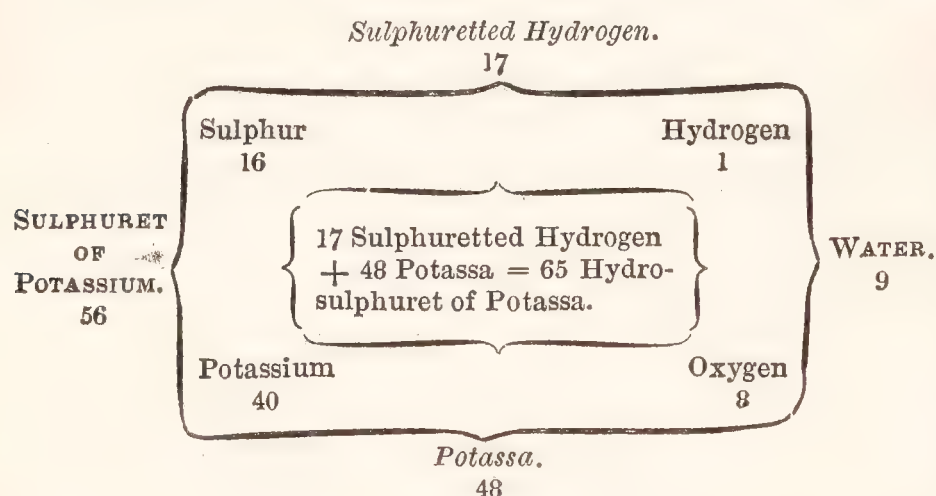
When potassiamide is heated out of contact of air, ammonia is evolved, and a grey substance remains, which is a compound of potassium and nitrogen = NK_3 ; this substance has been little examined; its formation may be thus represented: $3 [K, NH_2] = 2NH_3 + NK_3$. It effervesces when acted on by water, forming ammonia and potassa. $NK_3 + 3HO = 3KO + NH_3$.

POTASSIUM AND SULPHUR. SULPHURETS OF POTASSIUM. When potassium and sulphur are heated together in an exhausted tube, the sulphur not being in excess, intense action ensues, attended by the vivid combus-

tion of the potassium, and a brownish-grey compound results; when proper proportions of the materials are used, this is *protosulphuret of potassium*, KS. The same compound is obtained by heating atomic proportions of sulphate of potassa and charcoal (lamp-black), in which case if there be excess of lamp-black, the product is pyrophoric. Protosulphuret of potassium is also formed by passing hydrogen through a red-hot tube containing sulphate of potassa; water is formed in consequence of the deoxidizement, by the hydrogen, of the acid and of the potassa. In this case 1 equivalent of sulphate of potassa requires 4 of hydrogen, and 4 of water and 1 of sulphuret are the results. $\text{KO},\text{SO}_3 + 4\text{H} = \text{KS} + 4\text{HO}$. Thus procured it is a dark reddish-brown deliquescent substance, fusible at a heat below redness, of a caustic and sulphurous taste, soluble in water and alcohol, and when heated by the blowpipe, becomes incrustated with sulphate of potassa. This compound consists of

Potassium	1	...	40	...	71.4
Sulphur	1	...	16	...	28.6
<hr/>					
Protosulphuret of potassium	1		56		100.0

When sulphuret of potassium is put into water, it is generally assumed that it yields a solution of *hydrosulphuret of potassa*, KO,HS , in



consequence of the decomposition of one proportional of water, by one of the sulphuret, as shown in the annexed diagram: but Berzelius does not admit the decomposition of water in these cases, but considers the solution as containing the undecomposed sulphuret.

The aqueous solution of protosulphuret of potassium is alkaline, and is decomposed by acids, without any deposition of sulphur, sulphuretted hydrogen being evolved.

A similar compound may be obtained by passing sulphuretted hydrogen through an aqueous solution of potassa, and if this be carefully evaporated in a retort so as to exclude air, it forms colorless prismatic crystals; which, independent of water of crystallization, are considered as containing

Potassa	1	...	48	...	73.85
Sulphuretted hydrogen	1	...	17	...	26.15
<hr/>					
Hydrosulphate of potassa	1		65		100.00

HYDROSULPHURET OF POTASSIUM. KS,HS . When potassium is heated in sulphuretted hydrogen gas it burns, and the gas diminishes in volume. During this action the potassium decomposes 1 proportional of the gas, evolves hydrogen, and combines with its sulphur to form sulphuret of

potassium, which, uniting without decomposition with another proportional of the gas, forms a compound of

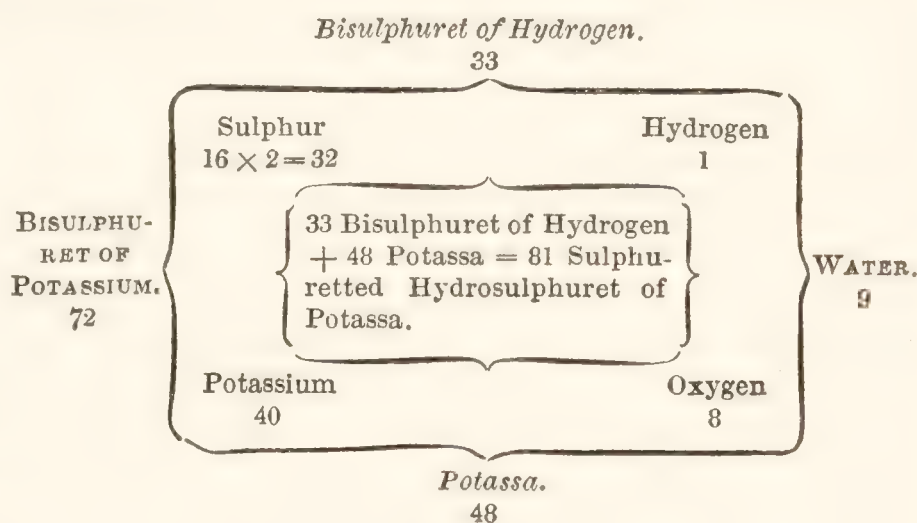
Sulphuret of potassium.....	1	56	76·71
Sulphuretted hydrogen.....	1	17	23·29
<hr/>					
Hydrosulphuret of potassium	1		73		100·00

It is to such compounds that the term *sulphur salts* properly applies. This hydrosulphuret yields with water a colorless solution of bihydrosulphuret of potassa. $\text{KO}, 2\text{HS}$. When dilute acids are dropped into a solution of this hydrosulphuret, one volume of sulphuretted hydrogen is evolved, and no sulphur precipitated: when the solution is exposed to air, it absorbs oxygen, and becomes converted into hyposulphite of potassa.

BISULPHURET OF POTASSIUM. KS_2 . When 4 parts of potassium are heated with 3 of sulphur, a brown fusible crystalline substance is obtained, permanent at a red heat, and consisting of

Potassium	1	40	55·6
Sulphur	2	32	44·4
<hr/>					
Bisulphuret of potassium	1		72		100·0

This compound decomposes one equivalent of water, and forms a yellow solution of sulphuretted hydrosulphuret of potassa, or of a compound of potassa with bisulphuretted hydrogen, KO, HS_2 , as in the annexed diagram.



The solution therefore contains

Potassa.....	1	48	59·3	}	Potassium	1	40
							Oxygen	1	8
							Sulphur....	2	32
							Hydrogen	1	1
Bisulphuret of hydrogen	1	33	40·7					
	<hr/>		<hr/>		<hr/>					
	1		81		100·0				1	81

When the dilute acids are added to this aqueous solution, sulphuretted hydrogen is evolved and sulphur precipitated in a peculiar white state, (*milk of sulphur*, see p. 382,) hydrated according to Thomson, but containing, according to Rose, a little bisulphuretted hydrogen; but if a *strong* solution of it be poured into hydrochloric acid, a viscid substance falls, which is bisulphuretted hydrogen (see page 410). Exposed to air, this solution passes into a hyposulphite, and sulphur is deposited.

The above compounds of sulphur and potassium are both permanent at high temperatures; but these unite indefinitely with sulphur by fusion at a moderate heat, and produce compounds in which the subsulphurets appear to act as bases to the supersulphurets. Berzelius describes seven sulphurets of potassium, in which 1 proportional of metal is combined

respectively with 1, 2, 3, $3\frac{1}{2}$, 4, $4\frac{1}{2}$, and 5 proportionals of sulphur (*Ann. Phil., N.S.*, iv. 214), but the definite nature of these compounds seems open to some doubt: the last, however, or the *pentasulphuret*, is said to be obtained pure by passing sulphuretted hydrogen over sulphate of potassa at a red heat, in which case, KO, SO_3 and 4HS , yield KS_5 and 4HO .

POTASSA AND SULPHUR. When sulphur is fused with hydrate of potassa, the water of the hydrate evaporates, and the oxide of potassium is decomposed, giving rise, at a red heat, to sulphuret or bisulphuret of potassium (according to the quantity of sulphur used), and to hyposulphite (which becomes sulphate) of potassa. It does not appear that any sulphurous acid is in these cases evolved.

When anhydrous carbonate of potassa mixed with half its weight of sulphur is kept at a red heat till carbonic acid ceases to be evolved, the result, according to Berzelius, is a *tersulphuret of potassium*, KS_3 , mixed with sulphate of potassa; the elements concerned in the product are 4 atoms of potassa and 10 of sulphur, which yield 3 atoms of tersulphuret of potassium, and 1 of sulphate of potassa; or in symbols, $4\text{KO} + 10\text{S} = 3\text{KS}_3$, and KO, SO_3 . If sulphur and carbonate of potassa be made to react on each other at the lowest possible temperature, pentasulphuret of potassium and hyposulphite are the results: 3KO , and 12S , yield in this case 2KS_5 and $\text{KO}, \text{S}_2\text{O}_2$.

The *potassii sulphuretum* of the Pharmacopœia is a similar compound of sulphuret of potassium and sulphate of potassa, obtained by heating 1 part of sulphur and 3 of carbonate of potassa; or, according to Phillips, (*Translation of Pharmacopœia*,) 4 atoms of carbonate of potassa, heated with 4 of sulphur, yield 1 atom of sulphate of potassa and 3 of sulphuret of potassium, 4 atoms of carbonic acid being expelled; as in the following equation: $4[\text{KO}, \text{CO}_2] + 4\text{S} = 3\text{KS} + [\text{KO}, \text{SO}_3] + 4\text{CO}_2$.

The compounds obtained by fusing potassa, or its carbonate, with sulphur, were formerly designated *Livers of Sulphur*, in consequence of their colour; and the conversion of sulphate of potassa into liver of sulphur by the action of charcoal and heat, was an experiment instituted by Stahl in support of the phlogistic hypothesis. Exposed to air, these sulphurets deliquesce, and exhale a disagreeable smell; their taste is bitter, acrid, and nauseous. The general results of dissolving them in water have been above noticed.

When sulphur is boiled with the hydrosulphuret, or when excess of sulphur is boiled in solution of potassa, bihydrosulphuret of potassa may be obtained; but as this compound, when in solution, dissolves variable and apparently indefinite portions of sulphur, an uniform combination is not in this way easily obtainable. The aqueous solutions of sulphuret of potassium are excellent conductors of electricity.

HYPOSULPHITE OF POTASSA. **DITHIONITE OF POTASSA**, $\text{KO}, \text{S}_2\text{O}_2$, is formed by decomposing hydrosulphuret of potassa by sulphurous acid, and evaporating to a pellicle, when it forms acicular crystals, of a cooling bitter taste, and deliquescent. After careful drying, it takes fire upon elevating the temperature, and burns like tinder. Its solution readily dissolves moist chloride of silver; and when exposed to air becomes sul-

phite, and ultimately sulphate, of potassa. This salt is also formed when the alcoholic solution of sulphuret of potassium is exposed to air, and the adhering sulphuret washed from its crystals by alcohol: or by heating a solution of sulphite of potassa with sulphur (see p. 401.)

SULPHYPOSULPHATE OF POTASSA. TRITHIONATE OF POTASSA. $\text{KO}, \text{S}_3\text{O}_5$. According to Langlois (*Ann. Ch. et Ph.*, 3 Ser. iv. 77), when excess of sulphurous acid (purified by washing) is passed through a solution of pure carbonate of potassa, and the resulting solution of bisulphite of potassa mixed with sulphur and kept for three or four days upon a sand heat, below its boiling-point, sulphurous acid is disengaged, a little sulphate formed, and the liquor, at first yellowish, becomes colorless. When the operation is complete it is presumed that hyposulphite of potassa is formed, and obtained in crystals on filtering the hot liquor and setting it aside (see p. 402.) But on redissolving these crystals, in the smallest possible quantity of warm water, a little sulphur separates and the filtered solution yields prismatic crystals which do not possess the properties of an hyposulphite; their solution is not decomposed at common temperatures by dilute acids, nor are they decomposed by hydrochloric acid: when heated to redness they leave neutral sulphate of potassa, and are not altered by exposure to air.

When this salt is carefully decomposed by heat, it yields 23.76 of sulphurous acid, 11.88 of sulphur are separated, and 64.36 of neutral sulphate of potassa remain, so that the sulphur which it contains appears to be distributed into three portions, one of which is evolved, one contained in the sulphurous acid, and one in the sulphuric. The composition therefore of this salt may be represented by 1 atom of potassa, 1 atom of sulphuric acid, 1 atom of sulphurous acid, and 1 atom of sulphur: its formula is $[\text{KO} + \text{S}_3\text{O}_5]$ and it contains *per cent.* 34.84 base + 65.16 acid. Hence it contains a distinct acid of sulphur, which may be regarded as a compound of sulphuric and hyposulphurous acid $= [\text{SO}_3 + \text{S}_2\text{O}_2]$ or of hyposulphuric acid and sulphur $= \text{S}_2\text{O}_5 + \text{S}$. Its properties, Langlois considers in favor of the latter view, he therefore proposes to designate it *Sulphyposulphuric acid*, and its saline combinations *sulphyposulphates*. This acid does not precipitate the salts of baryta or lead; it may be isolated by means of the perchloric acid, and its distinctive character is its resolution by heat into the products above mentioned.

BISULPHURETTED HYPOSULPHATE OF POTASSA. TETRATHIONATE OF POTASSA. $\text{KO}, \text{S}_4\text{O}_5$. This salt has not been examined, but it may probably be formed in the same way as the corresponding *soda* salt (which see.)

SULPHITE OF POTASSA, KO, SO_2 or K, SO_3 , is formed by passing sulphurous acid into a solution of potassa, or of its carbonate, and evaporating out of the contact of air. Rhomboidal plates or prisms, or sometimes acicular tufts, are obtained, white, anhydrous, of a sulphurous taste, and soluble in about their weight of water. By exposure to air, they pass into sulphate of potassa. Sulphite of potassa consists of

Potassa	1	48	60
Sulphurous acid	1	32	40
<hr/>					
Sulphite of potassa.....	1		80		100

BISULPHITE OF POTASSA. $\text{KO}, 2\text{SO}_2$. According to Langlois (*Ann. Ch. et Ph.*, 3 Ser. iv. 77), this salt is formed when sulphurous acid is passed through a solution of carbonate of potassa till all carbonic acid is expelled and excess of sulphurous acid escapes. This solution may be converted into the neutral salt by the addition of carbonate of potassa, and the neutral sulphite boiled with sulphur, filtered, evaporated, and set aside in a dry place, yields, in the course of 24 hours, crystals of hyposulphite. (See PLESSY on the Hyposulphites and Trithionates, *Ann. Ch. et Ph.*, June, 1844.)

HYPOSULPHATE OF POTASSA. DITHIONATE OF POTASSA. $\text{KO}, \text{S}_2\text{O}_5$, or $\text{K}, \text{S}_2\text{O}_6$, is obtained by decomposing a solution of hyposulphate of baryta, by sulphate of potassa. It forms permanent crystals of a bitter taste, difficultly soluble in cold, but readily so in hot water. It is anhydrous. Its crystals are described by Levy (*Quarterly Journal*, xv. 285). It consists, according to Heeren (*Ann. Ch. et Ph.*, xl. 30), of

Potassa	1	48	40
Hyposulphuric acid	1	72	60
<hr/>					
Hyposulphate of potassa	1		120		100

SULPHATE OF POTASSA. KO, SO_3 , or K, SO_4 . This salt is the result of several chemical operations carried on upon a large scale in the processes of the arts. It may be formed directly by saturating diluted sulphuric acid by carbonate of potassa. It is the *sal de duobus* and *arcanum duplicatum* of the old chemists: the *potassæ sulphas* of the *London Pharmacopœia*. Its taste is bitter and saline. It generally crystallizes in short six-sided prisms, terminated by six-sided pyramids. The body of the prism is often wanting, and the triangular-faced dodecahedron results. These forms have been described by Levy (*Quarterly Journal*, xv. 285); they result, according to Phillips (*Trans. Pharm.*), from a primary right rhombic prism. According to Mitscherlich its primitive form is a rhombic octohedron, and it is isomorphous with seleniate, and also with chromate of potassa. The crystals obtained from a solution of the salt which has been previously fused, sometimes emit a yellow light in the act of formation, especially when it contains a little sulphate of soda. They are anhydrous. According to Gay Lussac, 100 parts of water at 32° dissolve 8.36 of this salt, and 25 parts at 212° . At 60° one part requires 11.6 of water for its solution. (REDWOOD.) In consequence of its difficult solubility, it is thrown down, in a white granular powder, when sulphuric acid is added to a moderately strong solution of potassa. It is insoluble in alcohol, and also in a solution of potassa of sp. gr. 1.35. (LIEBIG.) Exposed to a red heat, it decrepitates and melts, but is not decomposed. At very high temperatures it is volatilized. It is decomposed at a red heat by hydrogen, which carries away the oxygen both of the acid and of the potassa, and converts it into sulphuret of potassium. When fused with sulphur, this salt undergoes no change; the sulphur sublimes unaltered. (VAUQUELIN, *Ann. Ch. et Ph.*, v. 20.) Intensely heated with one-fifth its weight of powdered charcoal, it produces sulphuret of potassium. When about 2 parts of sulphate of potassa and 1 of lamp-black, intimately mixed in fine powder, are heated to redness in a coated phial, and great care taken to exclude the air during

cooling, a compound is obtained which takes fire upon exposure to air. It appears to contain a compound of potassium, which powerfully attracts oxygen, and thus evolves heat enough to inflame the charcoal and sulphur. Gay Lussac attributes the combustibility of common pyrophorus (see ALUMINA) to the presence of this compound.

Sulphate of potassa consists of

						Kirwan.	Dalton.
Potassa	1	...	48	...	54.5	...	55 3
Sulphuric acid	1	...	40	...	45.5	...	44.7
<hr/>							
Sulphate of potassa	1		88		100.0		100.0

It appears from Jacquelain's researches that sulphate of potassa forms compounds with nitric and phosphoric acids. When, for instance, it is dissolved in nitric acid a little nitrate and hydrated bisulphate of potassa are formed, together with a salt in oblique prisms of which the formula, according to Graham, is $\text{HO},\text{NO}_5 + 2 [\text{KO},\text{SO}_3]$: it fuses at 202° , and its specific gravity is 2.38.

When sulphate of potassa is dissolved in a concentrated solution of phosphoric acid a double salt is obtained in oblique hexahedral prisms: it fuses at 464° , and its specific gravity is 2.29. Its formula is $3\text{HO},\text{PO}_5 + 2[\text{KO},\text{SO}_3]$.

BISULPHATE OF POTASSA, $\text{KO},2\text{SO}_3$, is formed by heating in a platinum crucible 88 parts of sulphate of potassa with 49 of oil of vitriol. When 1 atom of sulphate is dissolved in from 3 to 5 atoms of oil of vitriol, and evaporated to crystallization, an anhydrous bisulphate first forms in acicular crystals, but in a few days it liquifies and is converted into rhomboidal hydrated crystals. The acicular anhydrous crystals fuse at 410° . Their specific gravity is 2.27. The hydrated crystals are either *rhomboidal*, fusing at 386° , sp. gr. 2.16, or *fibrous and silky*. (JACQUELAIN, *Ann. Ch. et Ph.*, LXX. 311.) Graham terms the hydrated salt, *sulphate of water and potassa*, and represents it by $\text{HO},\text{SO}_3 + \text{KO},\text{SO}_3$. This salt is not decomposed below redness; at a red heat it gives out sulphuric acid, sulphurous acid, and oxygen, and is converted into the neutral salt. It is soluble without decomposition in about half its weight of boiling water, but by larger quantities of water it is more or less resolved into neutral sulphate and acid. The anhydrous bisulphate is apparently isomorphous with the bichromate of potassa: their composition is not easily reconciled with the binary or salt-radical theory, or with the doctrine of the constitutional neutrality of salts. (See GRAHAM, *Elements*, p. 328.) These bisulphates consist of

Jacquelain.										Jacquelain.					
Potassa	1	...	48	...	37.5	...	37.05	...	1	...	48	...	35.03	...	34.55
Sulphuric acid	2	...	80	...	62.5	...	62.95	...	2	...	80	...	58.39	...	58.40
Water	—	...	—	...	—	...	—	...	1	...	9	...	6.58	...	6.97
<hr/>															
Anhydrous bisulphate of potassa.....	1		128		100.0	100.00	Crystal- lised	137		100.00	100.00		100.00		100.00

Bisulphate of potassa is also formed by the distillation of 2 atoms of nitre and 1 of sulphuric acid, as in the usual process for obtaining *Nitric Acid*. (See p. 336.) It is often used as a substitute for dilute sulphuric acid for cleansing coin and other works in metal; and has a place in some *Pharmacopœiæ*.

SESQUISULPHATE OF POTASSA. $2\text{KO}, 3\text{SO}_3, \text{HO}$. This salt, or in its hydrated state, $2[\text{KO}, \text{SO}_3] + \text{HO}, \text{SO}_3$, described and analyzed by R. Phillips (*Phil. Mag., N.S.*, ii. 420,) is sometimes obtained as the residue of the distillation of equal weights of nitre and sulphuric acid, in filamentous crystals, consisting of

Potassa.....	2	96	42·67
Sulphuric acid.....	3	120	53·33
Water	1	9	4·00
<hr/>					
Crystallized sesquisulphate of potassa	1		225		100·00

AMMONIO-SULPHATE OF POTASSA. $[\text{KO}, \text{SO}_3; \text{NH}_4\text{O}, \text{SO}_3; 3\text{HO}]$, is obtained by adding ammonia to bisulphate of potassa, or by mixing solutions of sulphate of ammonia and sulphate of potassa, and setting aside to crystallize: it forms transparent prisms of a bitter taste: 100 of water at 60° dissolve 13. (LINK, *Crell's Annals*, 1796.) It consists of,

Sulphate of potassa.....	1	88	48·6
Sulphate of ammonia	1	57	31·5
Water	4	36	19·9
<hr/>					
Crystallized ammonio-sulphate of potassa....	1		181		100·0

PHOSPHURET OF POTASSIUM. KP , is a chocolate-brown compound, which rapidly decomposes water, evolving phosphuretted hydrogen gas. It is formed by cautiously heating atomic equivalents of potassium and phosphorus out of the contact of air; or by decomposing phosphuretted hydrogen by potassium, which, when heated in that gas, forms the phosphuret and evolves hydrogen. The composition of this phosphuret has not been accurately determined. When heated with potassium it appears capable of combining with an additional proportion of that substance, and forms a lead-colored compound. When these phosphurets are put into water, potassa, hypophosphite of potassa, hydrogen, and phosphuretted hydrogen, are the results.

By heating potassium with glacial phosphoric acid, Gay Lussac and Thenard obtained a brown compound which decomposed water: it was probably a mixture of phosphuret of potassium and phosphate of potassa.

HYPOPHOSPHITE OF POTASSA has been examined by Dulong. It is very deliquescent, and soluble in water and alcohol nearly in all proportions. When heated it evolves phosphuretted hydrogen and phosphorus, and is converted into phosphate of potassa. (*Ann. Ch. et Ph.*, ii. 142.) Rose prepared it by mixing a solution of hypophosphite of lime with one of carbonate of potassa, filtering, and evaporating to dryness: alcohol, digested upon the residue, takes up the hypophosphite of potassa. (*Quarterly Journal*, iv. 206.) The substance described by Grotthus (*Ann. de Chim.*, LXiv. 20), as resulting from the action of phosphorus upon a solution of potassa, is probably this hypophosphite. Wurtz prepares this salt by double decomposition, with hypophosphite of baryta and sulphate of potassa, evaporates the solution to dryness, and redissolves in hot alcohol: on cooling, it crystallizes in hexagonal tables, very deliquescent and very soluble in dilute alcohol, but less so in absolute alcohol, and insoluble in ether: they do not lose water at 212° : their formula is KO ,

PO_2HO , or, according to the views of Wurtz, $\text{KO}, \text{PH}_2\text{O}_3$. (*Ann. Ch. et Ph.*, Fevr., 1846.)

PHOSPHITE OF POTASSA is a soluble deliquescent uncrystallizable salt, insoluble in alcohol. When heated, hydrogen is evolved, and a neutral phosphate remains. (DULONG.) According to Wurtz (*Ann. Ch. et Ph.*, Fevr., 1846), phosphorous acid is bibasic, and the neutral phosphite of potassa is $2\text{KO}, \text{PO}_3, \text{HO}$, after having been dried at 538° . By evaporation in vacuo he obtained it in indistinct crystals. He has also described an *acid phosphite of potassa* obtained by dividing a solution of phosphorous acid into two parts, saturating one half with carbonate of potassa, then adding the other and evaporating in vacuo: it forms a foliated crystalline crust $= 2\text{KO}, 3\text{PO}_3, 7\text{HO}$.

PHOSPHATES OF POTASSA. 1. *Common Phosphate. a.* $3\text{KO}, c\text{PO}_5$. When 1 equivalent of phosphoric acid is fused with excess of carbonate of potassa, 3 equivalents of carbonic acid are evolved, so that 3 of potassa must have combined with the acid. This salt yields small acicular crystals, very soluble in water, (GRAHAM,) containing

					Saussure. (L. Gmelin.)
Potassa	3	144	66.6
c Phosphoric acid	1	72	33.4
	—		—		—
	1		216		100.0

β . $\text{HO}, 2\text{KO}, c\text{PO}_5$. This salt cannot be obtained in crystals. (GRAHAM.)

γ . $\text{KO}, 2\text{HO}, c\text{PO}_5$. This phosphate (formerly called *biphosphate* or *superphosphate*,) is formed by adding phosphoric acid to carbonate of potassa till the solution just reddens litmus paper, but on drying regains its blue color. On evaporation crystals are obtained, (BROOKE, *Ann. Phil.*, xxiii. 450,) which contain basic water, but no water of crystallization; they sustain a temperature of 400° , but, at a higher temperature, water goes off, and *metaphosphate* remains in a vitreous state. The crystals are very soluble in water but insoluble in alcohol, they taste sour, and redden litmus, but the blue returns on drying. (MITSCHERLICH, *Ann. Ch. et Ph.*, xix. 364.) They contain

					Mitscherlich.
Potassa	1	48	34.78
Phosphoric acid	1	72	52.18
Water	2	18	13.04
	—		—		—
Crystallized phosphate of potassa....	1		138		100.00

2. *Pyrophosphate.* $2\text{KO}, b\text{PO}_5$, is the result of the exposure of $\text{HO}, 2\text{KO}, c\text{PO}_5$, to a red heat: when dissolved in water it does not afford crystals, but reassuming an atom of water reverts to $\text{HO}, 2\text{KO}, c\text{PO}_5$ (GRAHAM.)

3. *Metaphosphate.* $\text{KO}, a\text{PO}_5$. This salt is probably formed when the basic water of $\text{KO}, 2\text{HO}, \text{PO}_5$, is expelled at a temperature exceeding 400° . If heated to redness, it becomes insoluble in water.

POTASSIUM AND SELENIUM. KSe . When these substances are heated together, they combine with intense action, and produce a grey crystalline compound, forming a deep brown solution with water, from which acids

evolve seleniuretted hydrogen and precipitate selenium. When selenium is heated with excess of potassium, an explosion ensues, and a compound is obtained which furnishes a red solution, and evolves hydrogen by the action of water. The odor and general characters of these compounds so much resemble those with sulphur, as not easily to be distinguished except by the brown and red colors of their solutions.

When powdered selenium is boiled in solution of potassa, a dark-brown solution of an hepatic taste and smell is the result, from which acids precipitate selenium. Fused with potassa, selenium produces seleniate of potassa and seleniuret of potassium.

POTASSA AND SELENIOUS ACID form, according to Berzelius, a neutral *selenite of potassa* (KO, SeO_2), a *biselenite* ($\text{KO}, 2\text{SeO}_2$), and a *quadriselenite* ($\text{KO}, 4\text{SeO}_2$). The first is difficultly crystallizable, somewhat deliquescent, and insoluble in alcohol. The second forms plumose crystals, very sparingly soluble in alcohol. The third is uncrystallizable. (*Ann. Ch. et Ph.*, ix. 257.)

SELENATE OF POTASSA. KO, SeO_3 . This salt may be obtained by fusing nitre with selenium or selenious acid, or by saturating the selenic acid by potassa. From the statement of Mitscherlich it consists of

						Mitscherlich.
Potassa	1	48	42·9 42·16
Selenic acid.....	1	64	57·1 57·84
<hr/>						<hr/>
Seleniate of potassa.....	1		112		100·0	100·00

According to the same authority, the seleniates and the sulphates are isomorphous, the form and optical properties of seleniate of potassa resembling those of the sulphate. (*Ann. Ch. et Ph.*, xxxvi. 104.)

POTASSIUM AND CARBON. When potassa is decomposed at high temperatures by carbon, a black substance remains in the retort, which is probably a *carburet of potassium* = KC . It is sometimes explosive by friction; it takes fire upon water; and if plunged into that fluid evolves carburetted hydrogen. It is probable that several of the pyrophoric charcoals contain potassium.

POTASSIUM AND CARBONIC OXIDE. When dry carbonic oxide gas is passed over potassium heated nearly to redness, a dark-colored compound is formed, which has been called an *oxicarburet of potassium*; it was first examined by L. Gmelin. The same compound has already been mentioned as forming a grey powder in the process of obtaining potassium by the action of charcoal on carbonate of potassa. It appears to consist of potassium and carbonic oxide, and has been represented by the formula $\text{K}_3, 7\text{CO}$: or $\text{K}_3, \text{C}_7\text{O}_7$: it is inflammable, and when in contact of water it yields carburetted hydrogen, and a dark-orange colored solution, in which a red powder is suspended, separable by filtration. The red powder is a compound of potassa with an acid, which Heller has succeeded in isolating, and which from the red color of its salts has been called *Rhodizonic acid*, (from $\rho\acute{o}\delta\iota\zeta\epsilon\upsilon\nu$, to redden); the filtered solution yields, when evaporated, a yellow potash salt, the acid of which, from the yellow colour of its combination, has been termed *croconic acid*, (from

κρόκος, saffron,) and the mother-liquor retains oxalate and carbonate of potassa.

Rhodizonic Acid. $C_7O_7, 3HO$? is obtained by pouring alcohol on the rhodizionate of potassa, and then adding sulphuric acid diluted with half its weight of water, and digesting in a gentle heat; sulphate of potassa and a colorless solution of the rhodizonic acid, are the results: the latter, on evaporation, gives small colorless crystals of a sour astringent taste, and sustaining a temperature of 212° without change, but decomposed at higher temperatures. The products of its decomposition have not been examined, but the *rhodizionate of lead*, analysed by Thaulow, is $3PbO, + C_7O_7$, so that the acid is regarded as tribasic. Although the hydrated acid is colorless, all its salts are red, and when crystallized, green by reflection.

Croconic Acid. C_5O_4, HO . When a solution of an alkaline rhodizionate is heated, oxalate and croconate of the base are produced; $3KO, C_7O_7$ becoming KO, C_2O_3 ; KO, C_5O_4 ; and KO . Gmelin obtained croconic acid by decomposing croconate of potassa by a mixture of alcohol and sulphuric acid, of sp. gr. 1.78, in the form of a yellow powder, little soluble in water, and giving by spontaneous evaporation, small yellow crystals, very sour and astringent, unchanged at 212° , but at higher temperatures becoming carbonised and burning without residue: soluble in alcohol and ether, and producing with bases yellow salts. Croconic acid is monobasic.

CARBONATE OF POTASSA. KO, CO_2 , is a salt of much importance in arts and manufactures, and is known in commerce in different states of purity, under the names of *wood-ash*, *pot-ash*, *pearl-ash*, *subcarbonate of potassa*: it was formerly known by other names, having reference to its sources; as *fixed nitre*, *salt of tartar*, *salt of wormwood*, *vegetable alkali*, &c.

It may be obtained directly, by passing carbonic acid into a solution of potassa, till saturated, evaporating to dryness, and exposing the dry mass to a red-heat; or indirectly, by burning purified *tartar* (bitartrate of potassa), lixiviating the residue, and evaporating to dryness. A mixture of purified tartar and nitre projected into a crucible heated to dull redness, also affords by its combustion a residue of carbonate of potassa, which may be obtained by lixiviation as the preceding. (*fixed nitre*.) When succulent vegetables are burned, their potassa-salts are for the most part converted into carbonate, hence the term *vegetable alkali*; and particular plants afford it in larger quantities than others, especially *wormwood*. The younger branches of trees afford more than the old wood, hence their selection as a source of *wood-ash*.

Carbonate of potassa is generally derived from two sources, for the use of the laboratory; namely from the carbonate of commerce, or from the bicarbonate. The carbonate of potassa of commerce is purified by lixiviating it with its weight of cold water; being more soluble than the salts which usually accompany it, these remain undissolved, and the solution, poured off, strained or filtered if necessary, and evaporated, leaves the carbonate of potassa. Or the crude carbonate may be dissolved in water, filtered, evaporated till the solution acquires the sp. gr. 1.52, and set aside in a cold place, when the greater part of the foreign salts are

deposited, and the solution of the carbonate may be poured off: with every precaution, however, when thus obtained, it is still impure, and contains chloride of potassium, and sulphate of potassa, and silica. When required pure for analytical purposes, carbonate of potassa is obtained by heating the crystallized bicarbonate to a temperature below redness, but sufficient to expel its water and half of its carbonic acid: the residue is then dissolved in cold water, and the filtered solution yields the pure salt, a portion of silica rendered insoluble by heating, remains upon the filter; if the bicarbonate be heated red hot, the silica expels carbonic acid to form a soluble silicate, and if not adequately heated, the solution will still contain silica. According to Juch, if a pound of pearl-ash be dissolved in a pint of distilled water, and 4 ounces of pulverised vegetable charcoal added, left for 24 hours, being often stirred and then filtered, it will not contain a trace of silica.

When equal parts of bitartrate and nitrate of potassa are burned in successive portions in an iron crucible, the residue was formerly called *white flux*, and *alkali extemporaneum*: when 2 parts of tartar is used to 1 of nitre, the whole of the charcoal is not consumed, and the product was called black flux; these compounds being much used in fusing or fluxing metallic ores*.

Carbonate of potassa is fusible without decomposition, at a red-heat; its specific gravity is 2.24: it is very soluble in water, which at 55° takes up nearly its own weight. According to Poggiale, 100 of water at 50° take up 83.12 of the anhydrous salt; 94.06 parts at 68°; 112.9 parts at 122°; 134.25 parts at 176°; 153.6 parts at 212°, and 205.11 parts at 275°, which is the boiling-point of the saturated solution. It deliquesces by exposure to air, forming a dense solution, formerly called *oil of tartar per deliquium*. Its taste is alkaline, and it has a strong alkaline action upon test-papers. It consists, in its fused or anhydrous state, of

						Vauquelin.	Dalton.
Potassa	1	48	68.6 67 68.9
Carbonic acid	1	22	31.4 33 31.1
<hr/>							
Carbonate of potassa.....	1		70		100.0	100	100.0

A saturated solution of carbonate of potassa in water contains about 48 *per cent.* of the salt, and has a specific gravity of 1.5. The following table, showing the quantity of dry carbonate of potassa in solutions of different specific gravities, is by Tünnermann. (GMELIN.)

Sp gr.	Per Cent.	Sp. gr.	Per Cent.	Sp. gr.	Per Cent.	Sp. gr.	Per Cent.
1.481 40.50	1.358 30.35	1.228 19.58	1.094 8.81
1.475 40.13	1.348 29.36	1.215 18.60	1.083 7.83
1.462 39.16	1.337 28.39	1.202 17.62	1.072 6.85
1.450 38.18	1.327 27.41	1.189 16.64	1.061 5.87
1.438 37.20	1.317 26.43	1.176 15.66	1.050 4.89
1.426 36.22	1.307 25.45	1.164 14.68	1.040 3.92
1.414 35.24	1.298 24.47	1.152 13.71	1.029 2.93
1.403 34.26	1.283 23.49	1.140 12.73	1.011 1.96
1.391 33.28	1.269 22.52	1.128 11.75	1.009 0.98
1.380 32.30	1.255 21.54	1.116 10.77	1.005 0.49
1.369 31.32	1.241 20.54	1.105 9.79		

* The *purified carbonate of potassa* of the shops should be perfectly soluble in twice its weight of cold water. It often contains *silica, sulphate of potassa, chloride*

If a solution of this carbonate be evaporated till of a specific gravity of 1.62 and then poured, whilst warm, into a tall cylindrical glass vessel, and suffered slowly to cool, it furnishes crystals in long rhomboidal tables, which are very deliquescent. The remaining mother-liquor, when cold, yields further crystals on evaporation, or when long kept: in the latter case, the crystals are rhombic octohedra. (BERARD, *Ann. Ch. et Ph.*, LXXI. 50. GIESE, *Scherer's Annalen*, iv. 294.) Fabbroni afterwards described these crystals, without being aware that they were previously known. (*Ann. Ch. et Ph.*, xxv. 5.) They consist of

						Giese.	Berard.		
Potassa	1	...	48	...	54.5	...	55	} ... 79.4	
Carbonic acid	1	...	22	...	25.0	...	25		
Water	2	...	18	...	20.5	...	20	...	20.6
<hr/>									
Crystallized carbonate of potassa	1		88		100.0		100		100.0

Carbonate of potassa is insoluble in alcohol, and is occasionally employed to deprive alcohol of water. Berzelius states, that if steam be passed over this salt in a red-hot tube, its carbonic acid is expelled, and hydrated potassa formed. A few of the metals, and charcoal at very high temperatures, decompose it with the production of potassium. The action of sulphur and of phosphorus upon this carbonate has already been noticed. At a white heat in an open vessel it slowly evaporates.

MANUFACTURE OF POTASH AND PEALASH. ALKALIMETRY. The consumption of carbonate of potassa in various manufactures is almost exclusively supplied by the combustion of vegetables, and consequently its production is limited to those countries which require clearing of timber, or where there are vast natural forests. The English market is chiefly supplied from North America. If vegetables growing in a soil not impregnated with sea-salt be burned, the residue, which is in the form of a brown saline mass, contains a large relative proportion of carbonate of potassa, and is commonly called *rough*, or *crude potash*. If it be again calcined so as to burn away the carbonaceous matter entirely, it becomes a white mass, generally termed *pearlash*.

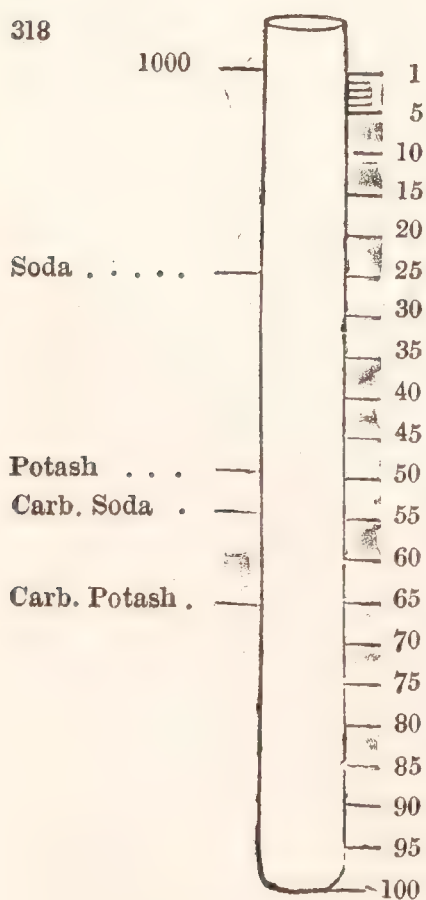
The pearlash of commerce contains a variety of impurities (especially chloride of potassium and sulphate of potassa), which render it of variable value. In general, its purity may be judged of by its easy solubility in water, 2 parts of which should entirely and easily dissolve 1 part of the salt without the aid of heat; the residue, if any, consists of impurities. The quantity of nitric acid of a given density, requisite to saturate a given weight, may also be resorted to as a criterion of its purity. 100 parts of nitric acid, specific gravity 1.36, will saturate 65.7 parts of dry

of potassium, and carbonate of lime. To detect these, dissolve a hundred grains in excess of nitric acid diluted with eight parts of water; the silica, if any be present, remains undissolved, or may be rendered insoluble by evaporation: separate the solution into three equal parts; to the first, add nitrate of baryta, which causes a precipitate of sulphate; collect, wash, and dry it; 100 parts are equivalent to 74 of sul-

phate of potassa: to the second, add nitrate of silver; 100 grains of the precipitate, washed and dried at a dull red-heat, are equivalent to 52 of chloride of potassium: to the third, add oxalate of ammonia, and dry the edulcorated precipitate at a heat of 300°; 100 parts are equal to 77 of carbonate of lime. When cyanide of potassium is present it may be detected by solution of iron with excess of hydrochloric acid.

carbonate of potassa, which are equivalent to 45 parts of pure potassa; or 355 grains of diluted sulphuric acid of the specific gravity of 1.141 exactly neutralize 100 grains of pure carbonate of potassa. Hence, if we dissolve 100 grains of the alkali to be examined, in six or eight parts of water, and gradually add the test sulphuric acid till we find, by the application of proper test-papers, that the alkali is exactly neutralized, we may deduce, from the weight of the acid consumed, the proportion of real carbonate present: for as 355 is to 100, so is the weight of the test-acid employed to that of the pure carbonated alkali present. To save trouble, the acid properly diluted may be put into a glass tube, so graduated as to show directly the value of the alkali by the quantity consumed in its saturation. Thus we find, by reference to the scale of equivalents, that 100 parts of carbonate of potassa are saturated by 70 of sulphuric acid, specific gravity 1.84. If, therefore, we put 70 grains of such acid into a tube divided into 100 parts, and fill it up with water, it follows that the quantity of carbonate of potassa existing in any sample of pearlash under examination, will be directly shown by the measure of such diluted acid required for saturation; 100 grains of the sample, if pure carbonate, would require the whole 100 measures of acid; but if only containing 50 *per cent.* of pure carbonate, the 100 grains would be saturated by 50 measures of the test-acid, and so on. Such graduated tubes are sometimes called *alkalimeters**.

The following directions respecting their construction and use, I abstract from FARADAY'S *Manipulation*. Let a tube, closed at one end (fig. 318), of about three-fourths of an inch internal diameter, and nine inches and a half in length, have 1000 grains of water weighed into it;



then let the space it occupies be graduated into 100 equal parts, and every ten divisions numbered from above downwards. At 23.44 parts, or 76.56 parts from the bottom, make an extra line a little on one side, or even on the opposite side to the graduation, and write at it with a scratching diamond, *soda*; lower down, at 48.96 parts, make another line and write *potash*; still lower at 54.63 parts, a third line marked *carb. soda*; and at 65 parts a fourth, marked *carb. potash*. It will be observed that portions are measured off, beneath these marks, in the inverse order of the equivalent numbers of these substances, and consequently directly proportionate to the quantities of any particular acid which will neutralize equal weights of the alkalis or their carbonates. As these points are of great importance, it will be proper to verify them by weighing into the tube first 350, then 453.7, then 510.4, and lastly 765.6 grains of water, which will correspond with the marks if

* Fresenius and Will have proposed an alkalimetrical process dependant under due precautions, upon the determination of the quantity of *carbonic acid* in the sample under examination. (*Chem. Gaz.*, October, 1843. BULLOCK.)

they are correct. Or the graduation may be laid down from the surface of the four portions of fluid when weighed in, without reference to where they fall upon the general scale. The tube is now completed, except that it should be observed whether the aperture can be perfectly and securely covered by the thumb of the left hand, and if not, or if there be reason to think it not ultimately secure, then it should be heated and contracted until sufficiently small.

Diluted sulphuric acid must now be prepared, to be used with the tube. When of a specific gravity of 1.1268, it will be very nearly, if not accurately, of the strength required; and this may be obtained by mixing 1 part by weight of oil of vitriol of specific gravity 1.82, with 4 parts of water. If, when cold, the specific gravity of this diluted acid be as above mentioned 1.1268, it must be nearly, if not exactly, of the strength required; but before being admitted into use, should be examined experimentally. Assuming it, however, as being absolutely correct, it will be found that a quantity measured into the tube up to any one of the four marks described, is sufficient to neutralize 100 grains of the dry alkali or carbonate set down at the mark; consequently, if water be added in the tube, thus filled up to any one of the marks, until the 100 parts are full, and the whole uniformly mixed, 1 part of such diluted acid will neutralize 1 grain of the alkali or carbonate named at the mark, up to which the tube was first filled with the acid of specific gravity 1.1268.

When a specimen of potash, barilla, or kelp, is to be examined by this instrument, 100 grains are to be weighed out, dissolved in warm water, filtered, the insoluble portion washed, and the solution added to the rest; by this process the alkali will be separated from carbonate of lime, or other insoluble matters, which otherwise might cause errors in the estimation. The alkaline solution is to be put into a basin on the sand-bath, and then the tube and acid prepared. For this purpose some of the acid, of specific gravity 1.1268, is to be poured into the tube until it rises up to the mark indicating the substance to be tested for; *potash* or *carbonate of potash* for the potash or pearlash of commerce, and *soda* or *carbonate of soda* for barilla or kelp: then water is to be added carefully, until the hundred parts are filled, and closing the tube with the finger, its contents are to be perfectly agitated and mixed.

The alkali in the basin is now to be neutralized with the acid in the tube. After having once placed the thumb of the left hand over the aperture of the tube, it is not to be again removed; but inverting the tube by turning the hand so that the thumb and the mouth of the tube are downwards, the acid is to be let out gradually into the alkaline solution, by relaxing the thumb and admitting a succession of small bubbles of air; the hot solution beneath is to be continually stirred, so as to mix the acid instantly with the whole, and the operator must proceed with increased caution as the point of neutralization is approached. Very small quantities of the acid may be added, by slightly relaxing the thumb so as to permit a minute quantity, less than a drop, to flow to its extremity, and touching it with a glass rod; the final adjustment may thus be made more accurately than by dropping the acid from the lip of the tube. The process must be carried on until the alkali is found by the test-papers to have been exactly neutralized: then the tube must be

inverted, the thumb removed, drawing its under surface over the edge of the tube, so as to leave as much as possible of the fluid that otherwise might adhere to it, and having allowed the sides to drain, it must be observed how many parts of acid have been used, the number of which will indicate the number of grains of the alkali or carbonate, contained in the 100 grains of the impure alkali operated with*.

With respect to the proper strength of the acid, it is to be examined in the following manner: crystals of bicarbonate of potassa are to be fused in a platinum crucible, the fluid poured out upon a clean, cold metal plate, and a piece of the resulting solid, estimated to be 70, 80, or 100 grains, weighed in water; in this way a known weight of pure carbonate of potash will be obtained in solution. The solution is then to be diluted, heated, and neutralized by acid from the tube diluted as before described, from the mark of carbonate of potassa. If it be found that as many parts of the acid have been used as of grains of the carbonate weighed out, the acid is of proper strength: if more acid has been used, it is too weak; if less has been sufficient, it is too strong. Suppose for instance that 100 grains of the salt (fused carbonate of potassa) had been used, and that 90 parts of the acid were sufficient; then these 90 parts ought to have occupied the 100, and consequently the 100 parts contain one-tenth too much acid, in consequence of the experimental acid itself containing one-tenth more than it ought to do. Hence the latter must be diluted with such a quantity of water as will make 9 volumes into 10, or by one-ninth its volume; for as the 90 parts used are to the 100 parts they ought to have occupied, so is any number of parts by volume of the acid under trial to the number of parts which it ought to occupy. The difference between the two last numbers will give the quantity of water in volumes, to be added to the acid expressed by the first of them, in order to correct it and make it of proper strength. On the contrary, if it were found that the 100 parts were insufficient, and that 10 parts more of similar acid were required, then there is too much water by one-eleventh of the whole in bulk, the correction for which would be one-tenth more of the 35 parts of acid put into the tube up to the mark 65 *carb. potassa*. This tenth is 3.5 parts, but as only a fifth of that or 0.7 parts is acid, therefore 0.7 parts by weight of the same oil of vitriol that was used before must be added for every 35 parts of the mixed acid. The correction in any other case may be easily made, by considering that the number of parts over a hundred which are necessary to saturate the 100 grains of carbonate of potassa, are proportionate to the quantity of oil of vitriol which must be added to bring the experimental acid to proper strength: thus if 136 parts of the diluted acid were used, then thirty-six hundredths more of the weight of oil of vitriol already used must be added; and the quantity of oil of vitriol that was added at first being known to be one-fifth by

* Some of the impure sources of potash and soda used in the arts, contain amongst other substances sulphuret and sulphite of alkali. Both these occasion errors in the mode of estimation above described, to obviate which MM. Welter and Gay Lussac (*Annales de Chimie*, xiii. 212) advise, that after the soluble parts have been separated

by water, a little chlorate of potash should be added to them, the whole evaporated and heated to redness. This converts the sulphuret and sulphite into neutral sulphate, and then upon re-dissolving the whole, the caustic and carbonated alkali may be ascertained as above described.

weight, the additional quantity required is easily ascertained. These corrections are not strictly accurate, but sufficiently so to meet even the exaggerated cases put of a difference of 10 parts, and to bring it within the limit of errors of experiment.

Sometimes instead of using test-papers, a little of the neutralized blue-cabbage liquor, or of infusion of litmus, may be put into the alkaline solution; the former immediately assumes a green tint: and by attending to the change effected by the addition of the acid, and noticing the point when blueness is again restored to the cabbage-color, or when the litmus becomes reddened, the indication of neutrality is sufficiently evident and accurate for general purposes. The test by papers, is, however, more precise.

A process of neutralization, quite the same in principle, may be adopted for the purpose of estimating the strength of *acids*, but from circumstances it is not often used, and being easily comprehended from the above directions, claims no further notice here.

BICARBONATE OF POTASSA. $\text{KO}, 2\text{CO}_2, \text{HO}$, or $\text{KO}, \text{CO}_2 + \text{HO}, \text{CO}_2$, is formed by passing a current of carbonic acid into a solution of the carbonate, or by subjecting the moist carbonate to excess of carbonic acid; for this purpose, Wöhler calcines tartar, moistens the cold carbonaceous mass with a little water, and saturates it with carbonic acid, which it absorbs rapidly, and with the evolution of heat, so that the vessel should be kept cool by immersion in water; the mass is then lixiviated with water at 140° , and the filtered solution deposits crystals of bicarbonate on cooling. Bicarbonate of potassa may also be obtained by the action of sesquicarbonate of ammonia on carbonate of potassa; pure ammonia is evolved.

Bicarbonate of potassa only exists in hydrated crystals: they belong to the oblique prismatic system; their primary form, which is a right oblique-angled prism, and their cleavages, have been described by Levy in the *Quarterly Journal*, xv. 286, and by Brooke. (*Ann. of Phil.*, N. S., vi. 42.) They are not deliquescent. Their taste is only slightly alkaline, and they require for solution about four parts of water, at 60° . Boiling water dissolves nearly its own weight of the crystals, but during the solution a portion of carbonic acid is evolved, and by long boiling, the salt becomes *sesquicarbonate*, or, according to some, reverts to the state of normal carbonate. Bicarbonate of potassa is nearly insoluble in absolute alcohol (soluble in 1200 of boiling alcohol. BERGMAN.) Exposed to a red-heat, it evolves carbonic acid and water, and carbonate of potassa remains. This salt was first observed by Dr. Wollaston to contain exactly twice the quantity of carbonic acid existing in the carbonate, and to part with exactly half its carbonic acid and the whole of its water, at a red heat. (*Phil. Trans.*, 1808.) It contains, according to Berard, 9 *per cent.* of water. It, therefore, consists of

						Berard.
Potassa	1	48	47.53 48.92
Carbonic acid	2	44	43.56 42.01
Water	1	9	8.91 9.07
<hr/>						
Crystals of bicarbonate of potassa	1		101		100.00	100.00

It is sometimes stated that during the saturation of silicated carbo-

nate of potassa with carbonic acid, the whole of the silica is precipitated; but this is not the case; during the crystallization of the salt, an additional deposition of silica generally ensues; but when the crystals have been redissolved, and a second or third time crystallized, the silica is almost entirely excluded.

The following proportions may be used for the preparation of bicarbonate of potassa upon the large scale: 100 lbs. of purified carbonate of potassa are dissolved in 17 gallons of water, which, when saturated with carbonic acid, yield from 35 to 40 lbs. of crystallized bicarbonate; 50 lbs. of carbonate of potassa are then added to the mother-liquor, with a sufficient quantity of water to make up 17 gallons, and the operation repeated. (HENNELL.)

The carbonate and bicarbonate of potassa are both decomposed by quick-lime, which deprives them of carbonic acid; hence the use of that substance in the process for obtaining pure *potassa*. They are also decomposed by the greater number of acids, which unite with the alkali, the carbonic acid being expelled with effervescence.

SESQUICARBONATE OF POTASSA. $2\text{KO}, 3\text{CO}_2$, or $\text{KO}, \text{CO}_2 + \text{KO}, 2\text{CO}_2$. When solution of bicarbonate of potassa is boiled till one-fourth of its carbonic acid is expelled, it is probable that this salt is formed. It may also be obtained by adding 131 parts of finely-powdered bicarbonate of potassa to 100 of carbonate, dissolved in water at 140° . On cooling the sesquicarbonate crystallizes. Rose doubts the existence of this salt, (*Poggend.*, xxxiv. 149,) and Berzelius supposes that the carbonate and bicarbonate may unite in more than one proportion. It was first noticed by Berthollet in 1809. A similar salt is mentioned by Thomson (*Princip. of Chem.*, II. 225,) who states it to consist of

Potassa	2	96	35.56
Carbonic acid.....	3	66	24.44
Water ...	12	108	40.00
<hr/>					
Crystallized sesquicarbonate of potassa	1		270		100.00

POTASSIUM AND CYANOGEN. CYANIDE OF POTASSIUM. CYANURET OF POTASSIUM. $\text{K}, \text{C}_2\text{N}$, or KCy , is obtained by passing a current of cyanogen over heated potassium; the metal absorbs the gas with ignition, and yields a yellowish grey compound. It is also formed by saturating a concentrated solution of caustic potassa with hydrocyanic acid, and boiling down in a retort till crystallization commences; the liquid is then poured into a porcelain capsule and heated till the residue is of a dull-red heat. Another mode of obtaining it consists in reducing the crystallized ferrocyanide of potassium to powder, drying it, and heating it to bright redness in a covered iron vessel, letting it cool excluded from air, bruising the porous fused mass, putting it into a glass funnel, moistening it with spirit of wine, and then lixiviating it with cold water; the first runnings are colorless and concentrated, and should be rapidly evaporated to dryness and fused in a porcelain capsule: or the fused mass may be boiled in weak alcohol, and on cooling the cyanide of potassium is deposited. A spirit of wine containing 60 per cent. of alcohol (sp. gr. .896) largely dissolves cyanide of potassium at its boiling-point, but lets nearly the whole fall on cooling; stronger or weaker

alcohol retains much more in permanent solution. According to Wigger, cyanide of potassium is also obtained by the transmission of hydrocyanic vapor from a mixture of ferrocyanide of potassium and sulphuric acid, into a concentrated alcoholic solution of potassa; as soon as it is saturated, the cyanide precipitates in the form of a crystalline powder. (LIEBIG.) In a subsequent communication to the Chemical Society, (*Mem.*, I. 94,) Liebig modifies the above process as follows: 8 parts of ferrocyanide of potassium, dried, powdered, and mixed with 3 of dry carbonate of potassa, are thrown into a red-hot earthen crucible, fused, and occasionally stirred, till the fused salt becomes colorless: the crucible is then removed from the fire, the contents stirred with a glass rod, and the clear salt poured off from the sediment, which is principally iron in a finely divided state. Thus obtained, the cyanide is mixed with a portion of cyanate, but the presence of the latter salt does not interfere with many of the uses to which cyanide of potassium is applicable, more especially the operations of electro-metallurgy. By this process 2 equivalents of ferrocyanide and 2 of carbonate are resolved into 5 of cyanide, 1 of cyanate, 2 of iron, and 2 of carbonic acid; $2[\text{FeK}_2\text{Cy}_3] + 2[\text{KO}, \text{CO}_2] = 5\text{KCy} + \text{KO}, \text{CyO} + 2\text{Fe} + 2\text{CO}_2$. Liebig and Trautwein recommend the use of this salt instead of the ferrocyanide for the preparation of hydrocyanic acid by distillation with dilute sulphuric acid. (See p. 513.)

When animal substances, such as horn or dried blood, are calcined at a red-heat, with half their weight of carbonate of potassa, so long as a blue flickering flame burns upon the surface, and after the mass has cooled, if it be lixiviated with a small quantity of water, a solution of carbonate with cyanide of potassium is obtained, which, when filtered, precipitated with acetate of lime, again filtered, and mixed with alcohol, yields a precipitate of cyanide of potassium. So also a current of nitrogen passed over a white-hot mixture of carbonate of potassa and charcoal yields cyanide of potassium, which settles in the colder parts of the tube in the form of a white powder, carbonic oxide being at the same time evolved. (FOWNES.) In these cases the union of the carbon and nitrogen to form cyanogen seems determined by the presence of the base. Cyanide of potassium is occasionally formed in iron furnaces where raw coal is used for fuel, with the hot blast. (CLARK.)

Cyanide of potassium should be carefully preserved out of the contact of air and water; it may be fused without decomposition, provided air be excluded, and is not changed by a red heat; but with the access of oxygen it becomes cyanate of potassa. $\text{KC}_y + 2\text{O} = \text{KO}, \text{CyO}$. After fusion it often crystallizes in cubes; its taste is pungent and alkaline, accompanied with the flavor of hydrocyanic acid. It is very soluble in water, and may be obtained from its aqueous solution in octohedral anhydrous crystals: it is little soluble in cold alcohol, so that the latter throws it down from its recent and cold aqueous solution: exposed to air it becomes moist and smells of hydrocyanic acid: it has an alkaline reaction, and is very poisonous. Its solution is decomposed by the acids, which resolve it into potassa and hydrocyanic acid; and when heated, its elements enter into new combinations, producing ammonia, and carbonic and hydrocyanic acids. Cyanide of potassium is a very powerful reducing agent as respects oxides and sulphurets, and as such is recommended by Liebig in mineral analysis; the oxides of copper, and those of

tin, iron, and lead, are immediately reduced when sprinkled into the fused cyanide. (*Mem. Chem. Soc.*, I. 97.)

When cyanide of potassium effervesces with the acids, it contains carbonate of potassa: a yellow tint indicates the presence of iron: if it blackens when calcined, it is contaminated by formiate of potassa. (LIEBIG.) It consists of

												Liebig.	
Carbon	2	...	12	...	18.25	} Cyanogen	1	...	26	...	39.50	...	40.24
Nitrogen	1	...	14	...	21.25								
Potassium	1	...	40	...	60.50		Potassium	1	...	40	...	60.50	...
<hr/>													
Cyanide of potassium	1		66		100.00		1		66		100.00		100.00

CYANATE OF POTASSA. KO, CyO , is obtained by carefully heating a mixture of 4 parts of powdered dry ferrocyanide of potassium, and 1 of peroxide of manganese to dull redness: when cold, the fused mass is powdered, and boiled in alcohol of 0.86, which dissolves the cyanate and deposits it on cooling. Cyanate of potassa is also formed by simply heating finely pulverized ferrocyanide of potassium to redness in an open iron pan, and continually stirring so as to expose it to the air; it absorbs oxygen, and when it begins to agglutinate in consequence of the fusion of the cyanate, it is powdered and digested in hot spirit of wine of sp. gr. 0.86. On cooling the filtered solution it deposits crystals of cyanate of potassa, the ferrocyanide being insoluble in alcohol. Another source of this salt, discovered by Liebig, consists in adding melam, ammeline, or ammelide, to hydrate of potassa fused in a silver basin.

Liebig also prepares cyanate of potassa by throwing powdered litharge into cyanide of potassium fused in a Hessian crucible; the oxide is reduced, and the lead first forms a fine powder mixed with the cyanate, but fuses into a button at a higher heat; the fluid mass is poured out, and the salt powdered and boiled with alcohol, from which it may be obtained in crystals. For the preparation of *artificial urea* the alcoholic purification is unnecessary.

This salt is decomposed both by water and acids, which convert the cyanic acid into carbonic acid and ammonia; in fact, by exposure to air it exhales ammonia, and, without changing form, becomes bicarbonate of potassa. It crystallizes in small plates like chlorate of potassa; tastes like saltpetre; is anhydrous; and in close vessels excluded from air and moisture, may be fused without decomposition. (WÖHLER. *Ann. Ch. et Ph.*, xx. 353, and xxvii. 196.) When fused with potassium it yields a mixture of cyanide of potassium and potassa; and with sulphur, a mixture of sulphocyanide of potassium, sulphuret of potassium, and sulphate of potassa. When triturated with oxalic acid, both being dry, oxalate of potassa is formed, and the evolved cyanic acid passes into that form of cyanuric acid which has been called *cyamelide* (p. 509.) Cyanate of potassa consists of

						Wöhler.	
Potassa	1	...	48	...	58.5	...	58.95
Cyanic acid.....	1	...	34	...	41.5	...	40.05
<hr/>							
Cyanate of potassa	1		82		100.0		100.00

SULPHOCYANIDE OF POTASSIUM. KC_2NS_2 . When 5 parts of dry ferrocyanide of potassium, 5 of sulphur, and 1 of carbonate of potassa, are

well mixed in fine powder and exposed to nearly a red-heat, the mixture fuses and takes fire; it should be stirred as long as it continues to burn, and kept for a few minutes in fusion. The residue, digested in hot water and filtered, furnishes a solution, which, evaporated to dryness, affords *sulphocyanide of potassium*; sulphuret of iron remains upon the filter. Sulphocyanide of potassium may be formed in the humid way by boiling 2 equivalents of finely powdered sulphur, in a solution of 1 equivalent of cyanide of potassium. (WIGGERS.) The sulphocyanide may be purified by digestion in alcohol, which dissolves it and leaves any carbonate of potassa that might have been mixed with it. The alcoholic solution when evaporated, leaves the pure salt, which, redissolved in water, and concentrated by evaporation, yields prismatic crystals which are of a cooling bitter taste, deliquescent, and anhydrous, being in form, taste, and fusibility, very analogous to nitre, very soluble in water, and produce during solution a considerable degree of cold.

In close vessels this salt fuses, and concretes on cooling into an opaque crystalline mass: heated in the air it is decomposed, and if moisture be present, carbonate of ammonia and sulphuret of potassium are formed. It is a compound of

						Berzelius.
Potassium	1	...	40	...	40·8	40·33
Sulphocyanogen	1	...	58	...	59·2	59·67
<hr/>						
Sulphocyanide of potassium	1		98		100·0	100·00

Its ultimate constituents, therefore, are

Potassium	1	...	40	...	40·8
Sulphur	2	...	32	...	32·7
Nitrogen	1	...	14	...	14·3
Carbon.....	2	...	12	...	12·2
<hr/>					
Sulphocyanide of potassium	1		98		100·0

Sulphocyanide of potassium forms a deep-red solution when added to persalts of iron, but no precipitate: with the salts of suboxide of copper it throws down white sulphocyanide of copper: it forms a yellow precipitate with acetate, and white with subacetate of lead; with nitrate of silver it gives a white curdy precipitate of sulphocyanide of silver. The other sulphocyanides are mostly soluble.

When solution of sulphocyanide of potassium is acted upon by chlorine a yellow powder is deposited, insoluble in water, alcohol, and ether, but soluble in sulphuric acid, from which it is thrown down by water: this substance has already been adverted to as *sulphocyanogen*, but its formula, according to Parnell, is $C_{12}H_3N_6S_{12}O$; or, regarded as a compound of sulphocyanogen, hydrosulphocyanic acid, and water, $= 4 [CyS_2] + 2 [HCyS_2] + HO$: when heated it evolves sulphur and bisulphuret of carbon, and leaves mellone $= C_6N_4$ or Cy_3N .

MELLONIDE OF POTASSIUM. $K_2C_6N_4$ is formed by heating mellone with potassium, or by dissolving it in concentrated solution of potassa. It may also be obtained by the mutual action of 4 atoms of sulphocyanide of potassium and 1 of chloride of antimony. (LIEBIG. *Chim. Org.*) According to Gregory, mellonide of potassium is best obtained by fusing at a low red heat in a covered iron crucible, dried ferrocyanide of potas-

sium with about half its weight of sulphur, and adding towards the end of the fusion about five *per cent.* of dried carbonate of potassa; the cooled mass is then boiled with water, and the filtered solution concentrated, till on cooling it forms a semisolid mass of minute acicular crystals, which are purified from sulphocyanide by washing with alcohol, in which the mellonide is insoluble. Mellonide of potassium may also be obtained by adding mellone to fused sulphocyanide of potassium, when by the decomposition of the sulphocyanogen an additional quantity of mellone is formed. In the first process a portion of mellone is also formed by the action of heat on the sulphocyanide of iron produced at the commencement of the fusion; and this mellone acts as in the second process, on the sulphocyanide of potassium, giving rise in so doing to an additional amount of mellone; hence the advantage of adding some carbonate of potassa, to prevent any loss of mellone. Lastly, mellonide of potassium may be prepared by adding two parts of subsulphocyanide of copper, to three of fused sulphocyanide of potassium. (*Outlines*, p. 311.)

Mellonide of potassium forms colorless acicular crystals, which are best obtained from a boiling solution in proof spirit: they are insoluble in alcohol, taste bitter, and contain 23·38 *per cent.* of water, the whole of which is given off between 250° and 300°. At a higher heat the salt fuses and concretes on cooling into a yellowish opaque crystalline mass: a red heat resolves it into nitrogen, cyanogen, and cyanide of potassium: if air be present, cyanate of potassa, and a less soluble salt, not hitherto examined, are the results. It consists of

Potassium.....	1	40	30·3
Mellone	1	92	69·7
<hr/>					
Mellonide of potassium	1		132		100·0

CYANURATE OF POTASSA. There are two cyanurates of potassa, represented by the formulæ $2\text{KO}, \text{HO}, \text{Cy}_3\text{O}_3$, and $\text{KO}, 2\text{HO}, \text{Cy}_3\text{O}_3$. The latter salt is obtained by adding to a boiling solution of cyanuric acid a quantity of potassa insufficient for its neutralization: it precipitates in difficultly soluble brilliant white cubes. When acetic or nitric acid are gradually added to a concentrated aqueous solution of cyanate of potassa, the displaced cyanic acid unites to the undecomposed cyanate, so as to form a cyanurate, which thickens the liquid; this cyanurate, when dissolved in caustic potassa, and precipitated by alcohol, yields the first-mentioned salt with two atoms of fixed base. It crystallizes in white needles: its aqueous solution has an alkaline reaction, and is resolved by evaporation into potassa and the cyanurate with 1 atom of fixed base. (LIEBIG.)

SELENIOCYANIDE OF POTASSIUM. $\text{K}, \text{NC}_2, \text{Se}_2$. Berzelius formed this salt by heating a mixture of ferrocyanide of potassium and selenium, and washing the fused mixture: by evaporation, anhydrous crystals of the *seleniocyanide* were obtained.

POTASSIUM AND BORON. When boracic acid is reduced by fusion with potassium, a brown mass results, which evolves hydrogen in water; probably, however, only from adhering potassium.

BORATE OF POTASSA. KO, BO_3 . When 1 equivalent of anhydrous boracic acid is fused at a white heat with 1 of dry carbonate of potassa, a

compound is obtained soluble in water, from which it crystallizes irregularly when evaporated to the consistence of syrup in vacuo: in the air it absorbs carbonic acid, even when dry.

						Arfwedson.
Potassa	1	...	48	...	57.83 58.16
Boracic acid	1	...	35	...	42.17 41.84
<hr/>						<hr/>
Borate of potassa	1		83		100.00	100.00

BIBORATE OF POTASSA. $\text{KO},2\text{BO}_3$. By adding an equivalent of boracic acid to a solution of the preceding salt, and evaporating, rectangular prisms are formed, very fusible, and including, according to Laurent, 27.8 per cent. of water. This salt reddens turmeric, tastes slightly alkaline, and fuses into a clear glass. It is easily soluble in hot and cold water. (GMELIN.)

						Laurent.	
Potassa	1	...	48	...	29.63	...	28.5
Boracic acid	2	...	70	...	43.21	...	43.7
Water	5	...	45	...	27.16	...	27.8
<hr/>						<hr/>	
Crystallized biborate of potassa.....	1		162		100.00		100.0

SEXBORATE OF POTASSA, $\text{KO},6\text{BO}_3$, is formed by adding boracic acid to a solution of the preceding salt till alkaline reaction ceases: it crystallizes in flat rhombic prisms, brilliant, and mostly hemitropic, slightly reddening litmus, permanent in the air, and sparingly soluble in cold, but abundantly in hot water: they contain 25.2 per cent. of water. (LAURENT, *Ann. Ch. et Ph.*, LXvii. 218.)

						Laurent.
Potassa.....	1	...	48	...	13.79 14.0
Boracic acid.....	6	...	210	...	60.31 60.8
Water	10	...	90	...	25.90 25.2
<hr/>			<hr/>			
Crystallized sexborate of potassa	1		348		100.00	100.0

BOROFLUORIDE OF POTASSIUM is obtained, according to Berzelius, by adding fluoboric acid to a solution of fluoride of potassium: a gelatinous precipitate falls, which, collected upon a filter, becomes opaque, and feels, whilst moist, like powdered starch. When dry, it has a bitterish taste; it does not redden litmus. 100 parts of cold water only dissolve 1.4 of this salt; but it is more soluble in boiling water, and, as the solution cools, it deposits it in small anhydrous crystals. It is sparingly soluble in boiling alcohol, and is deposited in crystals as the solution cools. It requires a high heat, long continued, for its decomposition, and is ultimately resolved into fluoboric gas and fluoride of potassium. (BERZELIUS.) It consists of

Potassium.....	1	...	40	...	31.49	} = {	Fluoride of potassium	1	...	59	...	46.45
Boron	1	...	11	...	8.66		Terfluoride of boron	1	...	68	...	53.61
Fluorine	4	...	76	...	59.85							
<hr/>						<hr/>						
Borofluoride of } potassium }	1		127		100.00			1		127		100.00

THE SALTS OF POTASSIUM are upon the whole readily soluble in water, though less so than the salts of ammonia. They produce a precipitate in solution of chloride of platinum. They are not changed by sulphuretted

hydrogen, nor by ferrocyanide of potassium. Added to sulphate of alumina, they enable it to crystallize, so as to form alum. The solution of potassa (and of most of its salts) is well characterized by the action of tartaric acid and of fluosilicic acid: a strong solution of tartaric acid added to a strong solution of potassa or of a salt of potassa causes no precipitate till the point of neutralization is exceeded; excess of the acid then produces a crystalline precipitate of *bitartrate of potassa*; when the solutions are dilute the precipitate is slowly formed and the crystals more apparent, but the effect is accelerated by stirring, and by the addition of a little alcohol; the precipitate is dissolved by the addition of hydrochloric, nitric, sulphuric, or oxalic acid, but not by tartaric, or by acetic acid. Solutions of carbonated and caustic potassa, soda, and ammonia, dissolve the precipitate with ease, but the addition of a small quantity of a strong acid reproduces it, and it is again dissolved by a greater quantity of the same acid. Fluosilicic acid produces a transparent gelatinous precipitate in solutions of potassa and of its salts, which is iridescent when it subsides, and dries into a white powder: free hydrochloric acid renders it opalescent. Perchloric acid, added to solutions of potassa and its salts, throws down a precipitate difficultly soluble in water, and insoluble in alcohol; an alcoholic solution of carbazotic acid produces in them a yellow crystalline precipitate. The neutral soluble salts of potassa may for the most part be heated to redness without suffering decomposition, especially if air be excluded. In using the test of chloride of platinum to detect potassa salts, the absence of ammoniacal salts must be previously ascertained, as they generally produce analogous effects upon that re-agent: or the platinum test may be applied after the salt has been subjected to a red-heat, by which the salts of ammonia will have been decomposed or evaporated. When chloride of platinum is used in quantitative analysis, it should be added in excess to the potassa solution, together with a drop or two of hydrochloric acid, and the mixture evaporated at 212° . The residue should then be washed with a mixture of equal parts of proof spirit and water, which removes everything except the potassiochloride of platinum.

When heated before the blowpipe, potassa salts communicate a purple or violet tinge to the flame, which is very characteristic. When a platinum wire is dipped into a solution of potassa or its salts, and after having been dried over a spirit lamp, is held in the flame, it communicates its peculiar purple tinge, and enables us to distinguish very minute traces of the alkali: the experiment should be made in a dark place, so at least that other light may not interfere; and the alcohol used in the lamp should be pure.

§ II. SODIUM. Na. 24.

SODIUM, (Natrium of the German chemists,) discovered by Sir H. Davy in 1808, was first obtained by the electrolysis of caustic soda, and afterwards by the action of iron at high temperatures, as in the decomposition of potassa: in this case the decomposition may be facilitated, according to Thenard, by fusing the soda with a small proportion of potassa; so that an alloy of sodium and potassium distils over, which may be decomposed by keeping it in an open vessel, covered with oil of

turpentine or with a film of naphtha; the potassium becomes oxidized, and the sodium remains pure and metallic. Sodium is now, however, always obtained by the action of charcoal at high temperatures, and the same arrangement is employed as described with respect to potassium: the iron bottle is charged with 1 pound of anhydrous and finely-powdered carbonate of soda, intimately mixed with 4 ounces of finely-powdered, and 8 ounces of coarsely powdered charcoal: or 66 ounces of crystallized carbonate of soda and 6 ounces of finely-powdered charcoal are well stirred and fused together, and heated to dryness in an iron pot, and 12 ounces of coarsely-powdered charcoal added. (GMELIN.) As sodium does not combine with carbonic oxide, the process is more productive than in the case of potassium. "Thus, in the Laboratory at Giessen, 1 pound of calcined acetate of soda (carbonate containing a little charcoal) mixed with a quarter of a pound of finely-powdered and half a pound of coarsely-powdered charcoal, and heated in a malleable iron bottle, yielded nearly 5 ounces of sodium; even then it was obvious that the result was capable of considerable improvement, the whole of the sodium present being about 7 ounces. From the extreme cheapness of carbonate of soda and the productiveness of the operation, sodium can be prepared far cheaper than potassium, and may in most cases be substituted for that metal, as its affinities are almost equally powerful. Should this metal ever be required on the large scale, it might be obtained for a price little, if at all, higher than that of zinc." (GREGORY.)

Sodium is soft, malleable, and easily sectile; it does not, like potassium, become brittle at 32° , but even at that low temperature, several globules may be welded together by pressure. Its specific gravity, according to Davy, is 0.9348; according to Gay Lussac and Thenard, it is 0.972 at 59° . In color it resembles silver, but instantly tarnishes on exposure to air. It softens at about 122° : it fuses at about 190° , and is volatile at a white heat, its vapor being colorless. It burns with a yellow flame when heated in contact with air, and requires the same cautions to preserve it from spontaneous oxidizement as potassium.

SODIUM AND OXYGEN. PROTOXIDE OF SODIUM. SODA. NaO . The affinity of sodium for oxygen appears to be somewhat less than that of potassium. When sodium is thrown upon water, it produces violent action, but the metal does not in general inflame, unless the quantity of water be very small, so as to diminish its cooling power; it inflames, for instance, if a thin slice of it be placed upon a piece of moistened paper, or if kept in one place on the surface of water: it also inflames on ice. By the quantity of hydrogen evolved during the action of sodium on water, we learn that soda consists of about 74.7 sodium, and 25.3 oxygen *per cent.*; and, if it be considered as the protoxide, the number representing the equivalent thence deduced for the metal will be 23.62. Other data give a number a little above 24. I shall therefore retain 24 as representing its atomic weight. (23.3 TURNER. 23.2 GMELIN.)

							Gay Lussac and Thenard.		Berzelius.		
							Davy.				
Sodium	1	24	75	74·6	74·7	74·34
Oxygen	1	8	25	25·4	25·3	25·66
<hr/>			<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
Soda	1		32		100		100·0		100·0		100·00

Anhydrous soda is obtained in the same way as anhydrous potassa, and resembles it in appearance, but is less fusible and less volatile.

PEROXIDE OF SODIUM. SESQUIOXIDE OF SODIUM. By heating sodium in oxygen, it burns vividly, and a yellowish-green *peroxide* is formed, which, by the action of water, evolves oxygen, (as is the case with peroxide of potassium,) and produces a solution of the protoxide. Peroxide of sodium is composed, according to Davy, of 2 atoms of sodium and 3 of oxygen, (Na_2O_3), but according to Millon it consists of 1 of sodium and 2 of oxygen. (NaO_2 .) Gmelin thinks that the peroxide, when obtained pure, will probably be NaO_3 , corresponding with the peroxide of potassium.

SUBOXIDE OF SODIUM is obtained as the suboxide of potassium; it is grey, brittle, without lustre, and very inflammable. (DAVY. GAY LUSSAC and THENARD.)

HYDRATE OF SODA. CAUSTIC SODA, NaO,HO , as it usually occurs in the laboratories, is obtained from the *carbonate*, by the action of lime, as described under the head *Potassa*. 2 parts of quick-lime to 3 of anhydrous carbonate, and to 10 or 12 of crystallized carbonate, is the quantity usually employed; this carbonate is more readily deprived of its carbonic acid than that of potassa, and being easily obtained in pure crystals, the solution of caustic soda is usually more pure than that of potassa, so that when boiled down with due precautions it affords a purer hydrate.

Hydrate of soda is white, opaque, brittle, and somewhat fibrous in its fracture; it is deliquescent; its sp. gr. is 2·0 (DALTON); it requires a red heat for fusion; and when intensely heated upon charcoal, as by the oxygen or oxyhydrogen blowpipe, it evaporates and tinges the flame yellow. It has the same general characters as hydrate of potassa: like it, it retains water at a red heat, and is deprived of it by the same means. It is very soluble in water and alcohol, and consists of

						Davy.	
Soda	1	...	32	...	78·1	...	77·1
Water	1	...	9	...	21·9	...	22·9
<hr/>			<hr/>		<hr/>		<hr/>
Hydrate of soda	1		41		100·0		100·0

Like potassa, it may be obtained in crystals from its concentrated aqueous solution, containing a larger relative quantity of water.

The following table by Dalton shows the proportion of anhydrous soda in solutions of different specific gravities:

Specific gravity of solution.	Dry Soda per cent. by weight.		Boiling- point.	Specific gravity of solution.	Dry Soda per cent. by weight.		Boiling- point.		
1·85	63·6	600 ^o	1·36	26·0	235 ^o
1·72	53·8	400	1·32	23·0	228
1·63	46·6	300	1·29	19·0	224
1·56	41·2	280	1·23	16·0	230
1 50	36·8	265	1·18	13·0	217
1·47	34·0	255	1·12	9·0	214
1·44	31·0	248	1·06	4·7	213
1·40	29·0	242					

Hydrated soda is distinguished from hydrated potassa, by forming an *efflorescent* paste when exposed to the atmosphere: potassa, under the

same circumstances, *deliquesces*. If *excess* of tartaric acid be added to a solution of soda, there is no precipitation; but in solution of potassa it occasions a crystalline deposit of a number of minute crystals. Solution of soda occasions no precipitate when added to solution of chloride of platinum, but solution of potassa occasions a yellow precipitate. In combination with acids it produces a perfectly distinct class of salts, well marked by their forms, ready solubility, and atomic relation to water. A solution of 1 part of antimoniate of potassa in 100 of water is recommended by Wachenroder, as a good precipitant of soda salts. (*Chem. Gaz.*, November, 1843.) Its affinity for the acids is a little inferior to that of potassa.

CHLORIDE OF SODIUM. SEA SALT. MURIATE OF SODA. NaCl. Sodium when heated in chlorine burns vividly, and produces this compound. It consists of

						Ure.	Longchamp.		
Sodium.....	1	24	40	39.98	39.767
Chlorine	1	36	60	60.02	60.233
<hr/>									
Chloride of sodium	1		60		100		100.00		100.000

Chloride of sodium is decomposed when heated with potassium: sodium and chloride of potassium are the results. (DAVY.)

When hydrate of soda is heated in chlorine, oxygen and water are evolved, and chloride of sodium formed; when heated in hydrochloric acid gas, the water of the hydrate is first expelled, and then the oxygen of the soda combines with the hydrogen of the hydrochloric acid to form water, and the sodium and chlorine unite to form the chloride.

Common salt exists abundantly in nature both as a solid fossil (*sal gemme*), and in the ocean. (See *Magnesia*, in reference to the composition of sea water.) Small quantities of salt are also found in nearly all spring and river water. Extensive beds of it are found in Cheshire, where it is known under the name of *rock-salt*. From these sources the immense demands are supplied; that is, either by evaporating brine-springs, or sea-water, or quarrying it from the mine.

When heated, chloride of sodium falls into pieces with a crackling noise, or *decrepitates*. At a red-heat it fuses without undergoing any decomposition, and on cooling concretes into a hard white mass; at a bright-red heat it sublimes in the air, and tinges flame of a blue color. It is nearly or quite insoluble in absolute alcohol, but dissolves in minute quantities in rectified, and in larger quantities in proof spirit. In the solubility of common salt in water there is this peculiarity, that it is taken up nearly in the same proportion by cold and by hot water; so that, although its solution deposits crystals during evaporation, it does not do so by cooling. According to Gay Lussac, 100 parts of water at 58° dissolve 36 of salt; at 140°, 37 parts; and at 225°, which is the boiling-point of a saturated solution, 100 parts of water dissolve 40.38. At 32° water dissolves rather more than at 60°. But according to Fuchs, pure chloride of sodium is equally soluble at all temperatures, 100 of water dissolving 37 of salt; or 1 of salt to 2.7 of water; such a solution corresponding to 1 atom of salt = 60, + 18 atoms of water = 162. The ice which forms at low temperatures in salt water is itself free from salt. Concentrated hydrochloric acid precipitates chloride of sodium from its

concentrated aqueous solution. When pure, chloride of sodium does not alter by exposure to air, though it is generally more or less deliquescent, from containing chlorides of magnesium and of calcium ; obtained by slow or spontaneous evaporation, it crystallizes in solid cubes; but when procured, as is usually the case, at a boiling heat, by removing its crystals from the surface of its solution whilst evaporating, it exhibits the form of a hollow quadrilateral pyramid. The crystals are anhydrous, though they often include a little interstitial water. Their specific gravity is 2.125. (2.557 MOHS.) A concise account of the different methods of manufacturing salt will be found in AIKIN's *Dictionary*, Art. MURIATE OF SODA. See also DUMAS, *Chim. app. aux Arts*, ii. 449, and URE, *Dict. of Arts and Manuf.* Dr. Henry states (*Phil. Trans.*, 1810) that the various forms under which salt is known in commerce, such as *bay-salt*, *fishery-salt*, &c., arise from modifications in the size and hardness of the grain, and not from any essential difference of composition. The following table includes his general results :

1000 Parts by Weight consist of

Kind of Salt.		Insoluble Matter.	Muriate of Lime.	Muriate of Magnesia.	Total Earthy Muriates.	Sulph. of Lime.	Sulph. of Magnesia.	Total Sulphates.	Total impurity.	Pure Muriate of Soda.
Cheshire Salt.	Brit. Salt fr. For. Bay Salt.									
	{ St. Ube's	9	trace....	3	3	23 ¹ / ₂	4 ¹ / ₂	28	40	960
	{ St. Martin's	12	do.	3 ¹ / ₂	3 ¹ / ₂	19	6	25	40 ¹ / ₂	959 ¹ / ₂
	{ Oleron	10	do.	2	2	19 ¹ / ₂	4 ¹ / ₂	23 ³ / ₄	35 ³ / ₄	964 ¹ / ₄
	{ Scotch (common)	4	—	28	28	15	17 ¹ / ₂	32 ¹ / ₂	64 ¹ / ₂	935 ¹ / ₂
	{ Scotch (Sunday)....	1	—	11 ¹ / ₂	11 ¹ / ₂	12	4 ¹ / ₂	16 ¹ / ₂	29	971
	{ Lymington (com.)	2	—	11	11	15	35	50	63	937
	{ Ditto (cat)	1	—	5	5	1	5	6	12	988
	{ Crushed rock.....	10	0 ¹ / ₁₆	0 ³ / ₁₆	0 ¹ / ₄	6 ¹ / ₂	—	6 ¹ / ₂	16 ³ / ₈	983 ¹ / ₄
	{ Fishery	1	0 ¹ / ₄	0 ³ / ₄	1	11 ¹ / ₄	—	11 ¹ / ₄	13 ¹ / ₄	986
	{ Common.....	1	0 ¹ / ₄	0 ³ / ₄	1	14 ¹ / ₂	—	14 ¹ / ₂	16 ¹ / ₂	983 ¹ / ₂
	{ Stoved	1	0 ¹ / ₄	0 ³ / ₄	1	15 ¹ / ₂	—	15 ¹ / ₂	17 ¹ / ₂	982 ¹ / ₂

According to Fuchs and Mitscherlich hydrated crystals of salt containing 6 and 4 atoms of water are formed when a saturated solution is exposed to a low temperature (between 14° and 5°). At temperatures above 14° they are resolved into small cubes and give off water. (FRANKENHEIM, *Poggend.* xxxvii. 638.)

Chloride of sodium is decomposed by moist carbonate of ammonia: bicarbonate of soda, sal-ammoniac, and free ammonia are formed; with moist carbonate of potassa, it yields chloride of potassium and carbonate of soda. In the process for obtaining hydrochloric acid it is decomposed by sulphuric acid. In this decomposition, the oxygen of the water of the sulphuric acid is transferred to the sodium of the salt, the chlorine of which combines with the hydrogen of the water to produce hydrochloric acid gas. The oxide of sodium unites with the dry sulphuric acid to produce sulphate of soda. $\text{NaCl} + \text{SO}_3\text{HO} = \text{NaO},\text{SO}_3 + \text{HCl}$. (See *Sulphate of Soda*). Chloride of sodium is also decomposed by nitric acid; effervescence ensues, chlorine tinged with nitrous acid is evolved, and, provided a sufficiency of nitric acid has been used, pure nitrate of soda remains on evaporation to dryness. When chloride of sodium is triturated with crystallized oxalic acid and heated, it is also decomposed,

hydrochloric acid is evolved, and oxalate of soda formed, so that when the residue is heated to redness, carbonate of soda remains. When chloride of sodium and ferruginous clay are heated together, the silica and alumina of the clay are vitrified by the soda of the salt, and its chlorine combines with the iron; it is upon this principle that it is used as a glaze for stone-ware; being thrown into the furnaces or ovens in which the articles are baked, it is volatilized, and decomposed upon their surfaces.

Common salt is of most extensive use as a preservative of food, and as a condiment, as a source of soda and of hydrochloric acid and chlorine, and for various agricultural and horticultural purposes. (*Quarterly Journal*, x. 52.) Glauber first obtained hydrochloric acid from it, and the existence of soda in it was first shown by Duhamel. Davy first demonstrated its true constitution.

CHLORIDE OF SODA. CHLORITE OF SODA. HYPOCHLORITE OF SODA. These names have been applied to a compound formed by passing chlorine into a cold and dilute solution of caustic soda, or by decomposing chloride of lime by carbonate of soda (as suggested by PAYEN, *Quart. Journ.*, N.S., i. 236). It is powerfully bleaching and smells of chlorine: exposed to air it absorbs carbonic acid and evolves chlorine, hence it may be used as a disinfectant. When heated, it undergoes changes similar to those produced by passing chlorine into a strong solution of soda, that is, chlorate of soda and chloride of sodium are formed. A formula in which chlorine is passed into a solution of *carbonate of soda* is given in the Pharmacopœia (*Liquor sodæ chlorinatæ*); it is more stable than the corresponding potassa compound, and therefore preferred for medical use as a disinfectant. It contains chlorite of soda, chloride of sodium, bicarbonate of soda, and carbonate of soda. (DUMAS.)

Labarraque's disinfecting liquid, which is essentially a hypochlorite, is made by passing chlorine into a solution of carbonate of soda. (See *Carbonate of Soda*, and *Hypochlorite of Potassa*.)

CHLORATE OF SODA, NaO,ClO_5 , or Na,ClO_6 , was procured by Che-nevix, (*Phil. Trans.*, 1802,) by the same process as chlorate of potassa, but not possessing less solubility than chloride of sodium the two substances are difficultly separable. Vauquelin obtained it by saturating chloric acid with soda. It is also formed by mixing strong solutions of bitartrate of soda and chlorate of potassa, when bitartrate of potassa precipitates, and chlorate of soda remains in solution, and may be obtained by evaporation, and purified by a second solution and crystallization. Its crystals are tetrahedral; its taste cooling and saline. It dissolves in three parts of cold water, and in somewhat less at 212° . It is more soluble in hydrated alcohol than chloride of sodium; hence that solvent is sometimes used to separate the two compounds. It is slightly deliquescent in very damp weather. It melts when heated, evolving oxygen, and a little chlorine, the residue being slightly alkaline. (GMELIN.) The crystals are anhydrous, and consist of

Soda	1	...	32	...	29·65
Chloric acid	1	...	76	...	70·35
<hr/>					
Chlorate of soda	1		108		100·00

PERCHLORATE OF SODA, NaO, ClO_7 , or Na, ClO_8 , is obtained by saturating soda with perchloric acid; it forms lamellar rhomboidal crystals, easily decomposed by heat but not by hydrochloric acid: they are deliquescent and soluble in alcohol. (PENNY. SERULLAS, *Ann. Ch. et Ph.* XLVI. 297.)

IODIDE OF SODIUM. NaI . Iodine and sodium act upon each other with the same phenomena as in the case of potassium. Iodide of sodium may also be formed by adding iodine to a solution of caustic soda and evaporating to dryness, and fusing the residue. It is contained in the mother-liquor of kelp, in the ashes of burned sponge, &c., and in those cases is resorted to as a source of iodine, and is decomposed by sulphuric acid and oxide of manganese (p. 286). When hydriodic acid is saturated with soda or carbonate of soda, and evaporated at a temperature between 105° and 120° , it affords anhydrous cubic crystals, resembling those of common salt. Iodide of sodium is less fusible than iodide of potassium: when intensely heated it becomes slightly alkaline, and is volatilized. 100 parts of water at 60° dissolve 173 of this iodide. It is also soluble in alcohol. It consists of

Sodium	1	24	16
Iodine	1	126	84
<hr/>					
Iodide of sodium	1		150		100

Large oblique rhombic prisms of *hydrated iodide of sodium* are deposited during the spontaneous evaporation of the aqueous solution of the iodide at common temperatures: they fuse when gently heated, and deliquesce in damp, but effervesce in dry air: they are soluble in 0.6 of water, and in hydrated alcohol. Their formula is $\text{NaI}, 4\text{HO}$. (MITSCHERLICH, *Poggend.*, xvii. 385.)

IODITE OF SODA? Iodine dissolved in weak solution of soda or carbonate of soda till it becomes brown, and exposed to spontaneous evaporation, deposits six-sided prismatic crystals of a pungent saline taste, neutral, and efflorescent. They are resolved by a little hot water or cold alcohol into iodide of sodium and iodate of soda, but are dissolved by cold water without decomposition. (MITSCHERLICH. PENNY.) Their formula is either $\text{NaO}, \text{IO}_2, 10\text{HO}$, or $\text{NaI}, \text{NaO}, \text{IO}_5, 20\text{HO}$ (MITSCHERLICH); or $3\text{NaI}, 2[\text{NaO}, \text{IO}_5,] + 38\text{HO}$. (PENNY.)

IODATE OF SODA, NaO, IO_5 , may be formed in the same way as iodate of potassa. Liebig obtains it as follows: Chlorine is passed through a mixture of 1 part of iodine and 10 of water till the iodine is dissolved: carbonate of soda is then added till the iodine is precipitated so as to render the liquor colorless, and this iodine is again dissolved by chlorine as before: the whole is then evaporated to about one-tenth its original bulk, and half its volume of alcohol added; this throws down iodate of soda which is to be washed with alcohol. (*Poggend.*, xxiv. 362. SERULLAS, *Ann. Ch. et Ph.*, xliii. 125; XLV. 59.) The aqueous solution of this salt yields crystals of varying composition dependent upon the mode of evaporation. (RAMMELSBERG, *Poggend.*, XLIV.) A warm saturated solution deposits crystals when slowly cooled to 40° in the form of silky needles containing 2 atoms (8.36 per cent.) of water, which they lose at

302°. Spontaneously evaporated at temperatures below 40° the crystals are eight-sided prisms containing 10 atoms of water (31·34 *per cent.*) but these are not permanent at temperatures above 40°, for they then become opaque and are an aggregate of the crystals with 2 atoms of water; they also undergo the same loss of water in the air. A warm dilute solution of the iodate deposits on cooling four-sided prisms, with 6 atoms of water (21·5 *per cent.* PENNY). Millon has described other modifications of these hydrates (BERZELIUS, *Lehrbuch*), according to whom they are all resolved into the bihydrated variety by drying in vacuo over sulphuric acid. The anhydrous salt fuses when heated, and evolves, even below redness, 24·45 *per cent.* of oxygen, with a little iodine, and leaves iodide of sodium and a little soda: it deflagrates on glowing charcoal, and detonates slightly when mixed with sulphur and struck by a hammer. (GAY LUSSAC.)

Rammelsberg has described a crystallizable compound of iodate of soda and chloride of sodium = $\text{NaO}, \text{IO}_5 + \text{NaCl} + 10\text{HO}$. (BERZELIUS.)

PERIODATE OF SODA. NaO, IO_7 . When chlorine is passed through a warm solution of caustic soda and iodate of soda till saturated, crystals are deposited on cooling of a basic salt = $2\text{NaO}, \text{IO}_7, 3\text{HO}$. By intense ignition they evolve oxygen and leave a mixture of 1 atom of soda with 1 of iodide of sodium. This salt, dissolved in periodic acid, yields, on evaporation, permanent colorless anhydrous crystals, easily soluble in water, of the neutral periodate = NaO, IO_7 . (MAGNUS and AMMER-MÜLLER, *Poggend.*, xxviii.)

BROMIDE OF SODIUM. NaBr . Sodium and bromine act upon each other with much intensity; the result is a fusible compound, soluble in water and in alcohol, and crystallizing at 86° in anhydrous cubes, but at lower temperatures in hexagonal tables, containing 26·37 *per cent.* of water. The taste of this salt is rather alkaline than saline. The *anhydrous bromide* consists of

Sodium	1	24	23·53
Bromine.....	1	78	76·47
<hr/>					
Bromide of sodium	1		102		100·00

And the hexagonal *hydrate* of

						Mitscherlich.
Anhydrous bromide	1	102	73·91 73·63
Water	4	36	26·09 26·37
<hr/>						
	1		138		100·00	100·00

Bromide of sodium may also be obtained by saturating hydrobromic acid with soda and boiling to dryness; or by the double decomposition of solutions of bromide of iron and carbonate of soda, boiling, filtering, and evaporating.

BROMATE OF SODA. NaO, BrO_5 . Prepared by saturating a solution of soda with bromine, and evaporating, by which the bromate separates and the bromide of potassium remains in solution: the first crystals may be redissolved and recrystallized. This salt (at temperatures above 40°) forms small brilliant anhydrous crystals, isomorphous with those of bro-

mate of potassa and of chlorate of soda, and soluble in 2·7 of water at 60°. When heated they fuse, give out oxygen, and leave bromide of sodium: they deflagrate on glowing charcoal, and detonate when mixed with sulphur and struck with a hammer. When the solution of this salt is crystallized at temperatures below 40°, it forms acicular four-sided prisms, which are efflorescent. (RAMMELSBURG, *Poggend.*, Lii. 85. MITSCHERLICH. LÖWIG, *Mag. der Pharm.*, xxxiii. 6.)

FLUORIDE OF SODIUM, NaF, is obtained by saturating hydrofluoric acid with soda, and evaporating to dryness; a white and difficultly fusible compound results, the aqueous solution of which, when pure, furnishes cubical crystals, and acts upon glass. 100 parts of water dissolve 4 of this fluoride, and it is not more soluble in hot than in cold water. It may also be obtained by mixing 10 parts of silicofluoride of sodium with 11·2 of dry carbonate of soda and sufficient water to form a thin paste, which, when boiled, evolves carbonic acid, and concretes. When cold, it must be powdered and boiled with more water as long as it effervesces; then filtered and evaporated (in silver, as it acts on glass,) till it crystallizes; the crystals must be redissolved and again formed, in order to separate adhering silica. During the formation of the crystals by slow evaporation, they exhibit the same luminous appearance as sulphate of potassa. (pp. 122 and 586.) When they retain any carbonate of soda, they are octohedral, but when pure, always cubic. They are insoluble in alcohol. (BERZELIUS, *Poggend.*, i. 13.) Fluoride of sodium consists of

Sodium	1	24	57·1
Fluorine	1	18	42·9
<hr/>					
Fluoride of sodium	1		42		100·0

Berzelius obtained a crystallizable compound of hydrofluoric acid and fluoride of sodium = NaF, HF, by leaving a solution of the fluoride in the acid to spontaneous evaporation: it forms small anhydrous rhombs, which, when heated, give off anhydrous fluoric acid, and leave 68 *per cent.* of fluoride of sodium.

HYPONITRITE OF SODA, NaO, NO₃, is obtained by heating nitrate of soda up to a certain point, dissolving in water, and crystallizing; nitrate of soda first separates, and afterwards hyponitrite. (See *Hyponitrite of Potassa.*)

NITRATE OF SODA. NaO, NO₅. The *cubic nitre* of old writers. This salt, which may be obtained by neutralizing carbonate of soda by dilute nitric acid, crystallizes in rhomboids (BROOKE, *Ann. Phil.*, 2nd series, v. 452), soluble in 3 parts of water at 60°, in its own weight at 123°, and in less than its weight at 212°. (DUMAS.) Berzelius says that one part dissolves in two of water at 60°, and Gay Lussac (*Cours de Chimie*, Paris, 1828) asserts that 100 parts of water at 32° dissolve 73 parts; and at 212°, 173 parts. Its solubility, as given upon the authority of Marx (THOMSON'S *System*, ii. 448), is as follows: 100 of water at 32° dissolve 80, at 50° 22·7, at 61° 55, and at 246° 218·5. So that, according to this account, its solubility at 32° is more than three times greater than at 50°. It has a cool sharp flavor, and is somewhat deliquescent in damp air, and therefore unfit for the manufacture of gunpowder. Berzelius found

a mixture of 5 nitrate of soda, 1 charcoal, and 1 sulphur, to burn three times more slowly than a similar mixture with nitrate of potassa: its flame is yellow. Nitrate of soda is often found in crude nitre, resulting partly, perhaps, from the decomposition of common salt. Large quantities of *native nitrate of soda* have been discovered in Peru, forming a stratum covered with clay and alluvium of many miles in extent, and it is now a considerable article of trade. It may be employed in fire-works, and used as a substitute for nitre (it being cheaper) in the manufacture of nitric acid, of sulphuric acid, and in other cases in which nitre is consumed. It is too expensive as a source of soda. It is frequently employed as a manure (*Journ. Agric. Soc.*, 1840-41), but with doubtful advantage, so far at least as regards wheat. Nitrate of soda is anhydrous, and consists of

						Wenzel.	Longchamp.
Soda	1	...	32	...	37.2	...	37.5
Nitric acid	1	...	54	...	62.8	...	63.25
<hr/>							
Nitrate of soda.....	1		86		100.0		100.00

SODIUM AND AMMONIA. SODIAMIDE. NaNH_2 . When sodium is heated in ammoniacal gas, hydrogen is disengaged, and an olive-colored fusible substance formed, composed apparently of sodium and amidogen. (GAY LUSSAC and THENARD, *Recherches*, i. 345. DAVY, *Phil. Trans.*, 1810, p. 24. See *Potassiamide*, p. 581.)

SODIUM AND SULPHUR. The account of the action of sulphur on potassium and potassa, and of sulphuretted hydrogen upon solution of potassa, applies generally to sodium and soda, and their corresponding compounds. Sodium and sulphur combine when gently heated, with vivid ignition, and form a *sulphuret of sodium*, NaS . And the same compound may be obtained by the decomposition of sulphate of soda at a red heat by hydrogen, or by charcoal. Dry sulphuretted hydrogen is abundantly absorbed by coarsely powdered caustic soda, with elevation of temperature and evolution of water. Sulphuret of sodium is composed of

Sodium	1	...	24	...	60
Sulphur	1	...	16	...	40
<hr/>					
	1		40		100

When this sulphuret is dissolved in water, or when solution of soda is half saturated by sulphuretted hydrogen, a colorless liquor is obtained, which, evaporated and cooled out of contact of air, gives colorless octohedral (rectangular prismatic) crystals of an hepatic, alkaline, and bitter taste. When heated in a retort they give off water and leave sulphuret of sodium; in the air they absorb moisture and gradually form sulphate of soda: they are very soluble in water, and less so in alcohol. They consist of

Kircher.					
Sodium.....	1	24	19.83	19.30	} = {
Sulphur	1	16	13.22	13.85	
Water	9	81	66.95	67.10	
<hr/>					
Crystals of hy-	} 1	121	100.00	Crystallized hydrosul-	
drated sulphuret					
of sodium					
<hr/>					
phuret of soda					
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BISULPHURET OF SODIUM, NaS_2 , is similarly constituted to the corresponding compound of potassium, and there are also other analogous supersulphurets.

HYPOSULPHITE OF SODA. DITHIONITE OF SODA, $\text{NaO}, \text{S}_2\text{O}_2$, is formed by exposing a solution of persulphuret of sodium to the atmosphere till it becomes colorless; or by adding a solution of carbonate of soda to hyposulphite of lime, and filtering. It crystallizes in silky tufts, and when the solution is concentrated, the whole concretes into a crystalline mass. It deliquesces in the air, but under a vacuum with sulphuric acid it effloresces. Its taste is bitter and nauseous; when heated it fuses, dries, and takes fire, deflagrating with a yellow flame. It is insoluble in alcohol, which precipitates it from its aqueous solution. It readily dissolves chloride of silver. (HERSCHEL, *Edin. Phil. Journ.*, i. 19.) The crystals include 5 atoms of water. Walchner prepares hyposulphite of soda as follows: 1 pound of dry carbonate of soda mixed with 10 ounces of powdered sulphur is heated in a porcelain dish, and stirred, when the sulphur fuses, to allow of contact of air: the sulphuret of sodium passes, under these circumstances, with slight incandescence, into sulphite of soda, which is dissolved in water, filtered, and boiled with flowers of sulphur: the filtered concentrated solution then yields crystals of the hyposulphite. (*Chem. Gaz.*, Aug. 1843, p. 524. *Ann. der Chem. und Pharm.*, May, 1843.) When perchloride of iron and hyposulphite of soda are mixed in solution, the results are protochloride of iron, chloride of sodium, and the bisulphuretted hyposulphite of soda of Fordos and Gélis. $\text{Fe}_2\text{Cl}_3 + 2[\text{NaO}, \text{S}_2\text{O}_2] = \text{NaO}, \text{S}_4\text{O}_5 + \text{NaCl} = 2\text{FeCl}$.

SULPHITE OF SODA, NaO, SO_2 , is obtained in the same way as sulphite of potassa; it is crystallizable in transparent four and six-sided prisms, soluble in four parts of water at 60° , and in less than its weight of boiling water. It consists of 32 soda + 32 sulphurous acid = 64. The crystals contain 8 atoms of water = 72. There is also a crystallizable *bisulphite of soda*, obtained by passing a current of sulphurous acid gas through a solution of carbonate of soda till fully saturated: it yields on evaporation four-sided rectangular prisms, having a sulphurous taste and smell, and reddening vegetable blues. (THOMSON.) Does not redden litmus. (GAY LUSSAC and WELTER.)

SULPHURETTED HYPOSULPHATE OF SODA. TRITHIONATE OF SODA. $\text{NaO}, \text{S}_3\text{O}_5$, has only been obtained in solution. (See the corresponding salts of potassa, p. 585.)

BISULPHURETTED HYPOSULPHATE OF SODA. TETRATHIONATE OF SODA. $\text{NaO}, \text{S}_4\text{O}_5$. This salt is most conveniently formed by the mutual decomposition of *bisulphuretted hyposulphate of baryta* and sulphate of soda: it is also obtained by the action of iodine on a solution of hyposulphite of soda, which is added till the solution begins to acquire color: the change may be thus represented: $2[\text{NaO}, \text{S}_2\text{O}_2] + \text{I} = \text{NaI} + \text{NaO}, \text{S}_4\text{O}_5$. FORDOS and GÉLIS, (*Ann. Ch. et Ph.*, Dec. 1842.)

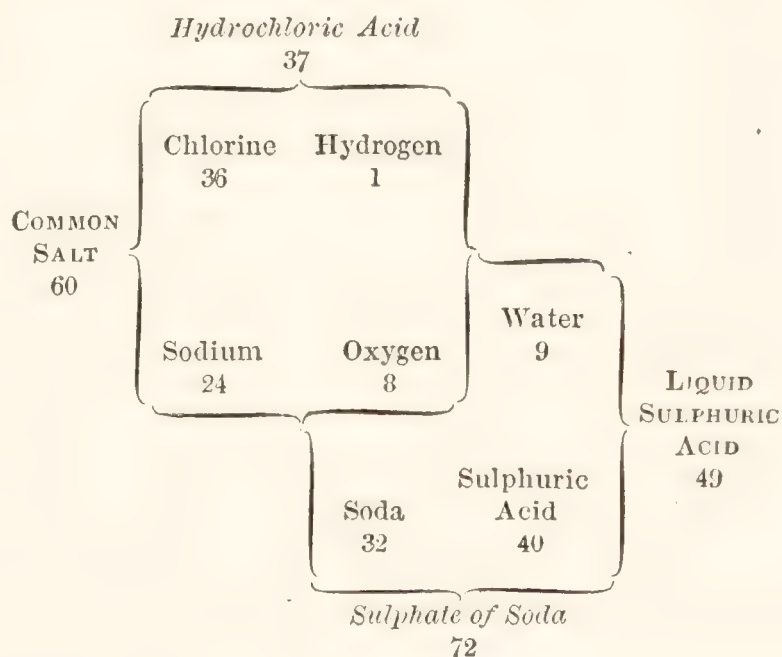
HYPOSULPHATE OF SODA. DITHIONATE OF SODA. $\text{NaO}, \text{S}_2\text{O}_5$, may be

obtained by decomposing hyposulphate of baryta by sulphate of soda; or hyposulphate of manganese may be decomposed by sulphuret of sodium, and the liquid evaporated to the point of crystallization: it forms transparent four-sided prisms of a peculiar bitterish taste, soluble in 2·1 of water at 60°, and in 1·1 at 212°, and insoluble in alcohol. According to Heeren (*Poggend.*, vii. 77), they contain

Soda	1	32	26·23
Hyposulphuric acid	1	72	59·02
Water	2	18	14·75
<hr/>					
Crystallized hyposulphate of soda	1		122		100·00

SULPHATE OF SODA. GLAUBER'S SALT. SAL MIRABILE. NaO, SO_3 , or NaSO_4 , is abundantly produced in various processes of the arts, by the action of oil of vitriol upon chloride of sodium. $\text{SO}_3, \text{HO}, + \text{NaCl} = \text{NaO}, \text{SO}_3 + \text{HCl}$: that is, chloride of sodium consists of 24 sodium + 36 chlorine: sulphuric acid consists of 40 dry acid + 9 water: the water of the acid, consisting of 1 hydrogen + 8 oxygen, is decomposed: its hydrogen is transferred to the chlorine to produce hydrochloric acid (1 hydrogen + 36 chlorine), and its oxygen unites to the sodium, forming soda (8 oxygen + 24 sodium). The 40 dry sulphuric acid unite to the 32 soda, to produce sulphate of soda, which will be represented by the number 72.

This decomposition is shown in the annexed diagram; the original substances being printed in capitals, the products in italics, and the components in common type: the numbers are the equivalent weights of 1 atom of the respective substances.



Sulphate of soda is also a natural product. Casaseca found anhydrous sulphate of soda (*Thenardite*) in the vicinity of Madrid; and Gimbernath, in the Canton D'Argovie in Switzerland. It occurs in many common springs and mineral waters. It is also found in the ashes of some plants (*Tamarix Gallica*), and in some of the animal fluids.

Anhydrous sulphate of soda may be obtained by drying the hydrated crystals upon a sand heat: they fall into a white powder, which reabsorbs water with the evolution of heat. When a hot concentrated solution of sulphate of soda is suffered to deposit crystals (at a temperature between 90° and 100°), they are anhydrous rhombic octohedra. (MITSCHERLICH, *Poggend.*, xii. and xxv. THOMSON, *Ann. Phil.*, xxviii. 401,) sp. gr. 2·462. 100 of water at 57°, dissolve 10·58 of this anhydrous salt, and the solution set aside to cool and crystallize, gives the common decahydrated crystals,

Fused sulphate of soda concretes on cooling into a foliated crystalline mass; sp. gr. 2·63. The anhydrous salt consists of

						Wenzel.	Longchamp.
Soda	1	...	32	...	44·4	44·3	43·9
Sulphuric acid	1	...	40	...	55·6	55·7	56·1
<hr/>							
Anhydrous sulphate of soda	1		72		100·0	100·0	100·0

The ordinary crystals (decahydrated sulphate of soda) are deposited from solutions cooled to common temperatures: they are large transparent striated prisms, belonging to the oblique prismatic system. (BROOKE, *Ann. of Phil.*, xxiii. 21. PROVOSTAYE, *Ann. Ch. et Ph.*, lxxviii. 354.) Sp. gr. 1·35. (THOMSON.) They are efflorescent, and by due exposure to dry air lose the whole of their water, crumbling into white powder, which, however, in very damp air, reabsorbs water with considerable increase of bulk. When gently heated, the crystals fuse, and at the same time deposit anhydrous sulphate: their taste is saline and very slightly bitter: they are insoluble in alcohol. The solubility of sulphate of soda in water follows a singular law, first observed by Gay Lussac. (*Ann. Ch. et Ph.*, xi.) After having increased rapidly to about the temperature of 92°, where it is at its maximum, it diminishes to 215°, and at that temperature the salt is nearly of the same solubility as at 87°.

At 32° 100 parts of water dissolve about 5 of anhydrous and 12 of crystallized salt.

50	”	”	10	”	26	”
60	”	”	11	”	31	”
70	”	”	16	”	48	”
77	”	”	28	”	99	”
87	”	”	43	”	215	”
92	”	”	50	”	322	”
104	”	”	48	”	291	”
122	”	”	46	”	262	”

This common crystals contain

						Berzelius.	Brandes and Firnhaber.
Soda	1	...	32	...	19·74	19·24	19·1
Sulphuric acid	1	...	40	...	24·69	24·76	24·4
Water	10	...	90	...	55·57	56·00	56·5
<hr/>							
Decahydrated sulphate } of soda	1		162		100·00	100·00	100·0

When crystallized sulphate of soda is dissolved in its weight of boiling water, and a flask filled with it and tightly corked up, no crystallization generally ensues: but upon opening the flask it either immediately crystallizes, or does so upon touching the solution with a solid body. This experiment has already been referred to (p. 10). It sometimes, however, happens that a portion of the salt does crystallize, forming quadrangular crystals, which become opaque on exposure, and which, for sulphate of soda, are peculiarly hard; Faraday (*Quart. Journ. Sc.*, xix. 52,) found these composed of

Dry sulphate of soda	1	...	72	...	50
Water	8	...	72	...	50
<hr/>					
Octohydrated sulphate of soda	1		144		100

Gay Lussac obtained a powerful pyrophorus, by igniting a mixture of lamp-black and dry sulphate of soda, analogous to that mentioned under

Sulphate of Potassa. (*Quart. Journ. Sc.*, iv. 208.) The decomposition of sulphate of soda for the manufacture of *carbonate of soda* is described under the latter salt.

BISULPHATE OF SODA. $\text{NaO},2\text{SO}_3$, is obtained by adding sulphuric acid to a hot solution of sulphate of soda. It crystallizes in rhombic prisms, soluble in twice their weight of water at 60° , and containing water of crystallization. (*LINK, Crell's Annals*, 1796.) When a crystal of bisulphate of soda is held in the candle, it melts like ice. This salt liquifies at 300° , and may be kept at that temperature without much loss of weight. Its specific gravity is 1·8. At the temperature of 60° , one hundred parts of water dissolve 92·72 of this salt, so that it is twice as soluble as crystallized sulphate of soda. Its taste is very acid. (*THOMSON, Ann. Phil.*, x. 439, 2nd Series.) An *anhydrous bisulphate of soda* may be obtained by gently heating together in a platinum crucible 10 parts of dry sulphate of soda, and 7 of sulphuric acid (specific gravity 1·84); the water of the acid escapes, and the residue may then be fused: it furnishes a very soluble but not a deliquescent salt, which, when distilled at a high temperature, affords *anhydrous sulphuric acid*. (*BERZELIUS.*) Graham represents the crystallized bisulphate by the formula $\text{HO},\text{SO}_3 + \text{NaO},\text{SO}_3$. According to Brandes the crystals contain 3, and to Thomson, 4 atoms of water.

SESQUISULPHATE OF SODA. $2\text{NaO},3\text{SO}_3$. According to Thomson (*Ann. of Phil.*, 2nd Series, x. 436), this salt is obtained when the residue after the decomposition of common salt by sulphuric acid in excess is dissolved in hot water and set aside; it usually forms the first crop of crystals; they are transparent prisms, firmer and harder than the common sulphate, of an acid taste, but neither deliquescent nor efflorescent. Their specific gravity is 2·226 at 63° . 100 of water dissolve 25 of this salt. When water saturated with it is set aside, crystals of the common sulphate are formed: it loses but little weight even at a red-heat: it is anhydrous, and consists of

Soda.....	2	64	34·78
Sulphuric acid.....	3	120	65·22
<hr/>					
Anhydrous sesquisulphate of soda....	1		184		100·00

A sesquisulphate of soda is obtained, according to Mitscherlich, by adding half an equivalent of oil of vitriol to sulphate of soda, and evaporating the solution till it attains the degree of concentration necessary for crystallization.

AMMONIOSULPHATE OF SODA. $\text{NH}_4\text{O},\text{NaO},2\text{SO}_3 + 4\text{HO}$, is a double salt, formed by saturating the bisulphate with ammonia, (*LINK, Crell's Annals*, 1796, i.) or by dissolving the two sulphates in atomic proportions and crystallizing: it yields transparent prisms with rhombic bases, of a bitter taste, consisting, according to Riffault, (*Ann. Ch. et Ph.*, xx. 432,) of

						Riffault.
Ammonia.....	1	17	9·77 9·678
Soda.....	1	32	18·39 18·550
Sulphuric acid.....	2	80	45·97 45·740
Water	5	45	25·87 26·032
<hr/>						
Crystallized ammoniosulphate of soda	1		174		100·00	100·000

SODIUM AND SELENIUM. The seleniuret of sodium has not been examined.

SELENITE OF SODA. NaO, SeO_2 , is very soluble and difficultly crystallizable. It tastes like borax. It is insoluble in alcohol, and not deliquescent. *Biselenite of soda*, $\text{NaO}, 2\text{SeO}_2$, is also very soluble: its solution when evaporated to the consistence of syrup forms clusters of radiated crystals. At a red-heat it fuses and gives off acid so as to become neutral. *Quadriseelenite of soda*, $\text{NaO}, 4\text{SeO}_2$, yields radiated crystals by spontaneous evaporation. (BERZELIUS.)

SELENIATE OF SODA. NaO, SeO_3 , may be obtained by deflagrating a mixture of selenium and nitrate of soda. It is isomorphous with sulphate of soda, and follows the same law with regard to its solubility in water, and water of crystallization.

PHOSPHURET OF SODIUM. NaP , possesses the general properties of the corresponding compound of potassium.

HYPOPHOSPHITE OF SODA. NaO, PO , is very soluble both in alcohol and water. (DULONG, *Ann. Ch. et Ph.*, II. 142.) It may be obtained by mixing hypophosphite of lime with a slight excess of carbonate of soda, filtering, evaporating to dryness, and digesting in alcohol, which dissolves the hypophosphite, and which by very careful evaporation may be obtained in prismatic crystals which are very deliquescent, and when heated evolve phosphuretted hydrogen.

PHOSPHITE OF SODA. NaO, PO_3 , forms rhombic crystals, very soluble in water and alcohol. (DULONG.) Insoluble in alcohol. (DUMAS.) According to Wurtz, the neutral phosphite is $= 2\text{NaO}, \text{PO}_3, 11\text{HO}$: he has also described an *acid phosphite* $= 2\text{NaO}, 3\text{PO}_3, 8\text{HO}$.

PHOSPHATES OF SODA. 1. *Tribasic phosphates*. There are, according to Graham, three phosphates of soda belonging to the tribasic class: these have been usually distinguished as *common* or *rhombic phosphate*, *subphosphate*, and *biphosphate*. The *ammoniophosphate* also belongs to this class.

a. *Common or rhombic phosphate*. $2\text{NaO}, \text{HO}, \text{cPO}_5 + 24\text{HO}$. This salt, (the *sal perlatum* of some old writers,) is obtained by saturating the impure phosphoric acid prepared from calcined bones by sulphuric acid, with carbonate of soda: the liquor is filtered, evaporated, and set aside to crystallize. The crystals form most readily in an alkaline solution: they are oblique rhombic prisms, (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 286,) always alkaline to test-paper, superficially efflorescent, and soluble in about 4 parts of cold and 2 of hot water. This salt has a slightly saline and alkaline flavor, and has been used in medicine as an aperient under the name of *tasteless purging salt*. Its specific gravity is 1.33. The crystals when moderately heated fuse in their water of crystallization; at a dull red-heat, the salt runs into a clear glass, which becomes opaque on cooling: (*pyrophosphate*.) It is deprived of half its alkali by hydrochloric acid, but not by acetic acid.

This form of phosphate of soda consists of

					Berzelius.	Clark.	Graham.
Soda.....	2	64	17.72	17.67	37.48	37.1
Phosphoric acid	1	72	19.94	20.33
Basic water.....	1	9	2.49	62.00	2.49	62.9
Water of crystallization	24	216	59.85	60.03
<hr/>							
Crystallized rhombic } phosphate of soda }	1	361	100.00	100.00	100.00	100.0

When a solution of this phosphate is evaporated at a temperature of 90° , it crystallizes according to Clark (BREWSTER'S *Journal*, vii. 311,) in a modified form, with only 14 atoms of water. When dropped into nitrate of silver, it forms a yellow precipitate.

β . *Subphosphate of Soda.* $3\text{NaO}, \text{cPO}_5 + 24\text{HO}$. When excess of caustic soda is added to a solution of the preceding salt, it yields on evaporation slender six-sided prisms, which are permanent in the air, soluble in 5 parts of water at 60° , and undergo watery fusion at 170° . The solution of this salt absorbs carbonic acid, and is deprived of one-third of its alkali by the weakest acid. This salt continues tribasic after exposure to a red heat. (GRAHAM.) It contains

					Graham.
Soda	3	96	25.00	24.70
Phosphoric acid	1	72	18.75	18.60
Water of crystallization	24	216	56.25	56.03
<hr/>					
Crystallized subphosphate of soda	1	384	100.00	99.33

γ . *Phosphate of Soda and Water. Biphosphate of Soda.* $\text{NaO}, 2\text{HO}, \text{cPO}_5 + 2\text{HO}$, is obtained by adding tribasic phosphate of water to a solution of the common phosphate, till it ceases to precipitate chloride of barium. The solution in cold weather affords crystals, of which the ordinary form is a right rhombic prism, having its larger angle of $93^{\circ} 54'$, but it also occurs in another right rhombic prism, isomorphous with binarsenate of soda. This biphosphate is very soluble, and has distinct acid reaction. (GRAHAM.) Like the preceding salts, it occasions a yellow precipitate of tribasic phosphate of silver, in solution of nitrate of silver. It consists of

					Graham.
Soda.....	1	32	22.86	73.76
Phosphoric acid	1	72	51.42
Basic water.....	2	18	12.86	26.24
Water of crystallization.....	2	18	12.86
<hr/>					
Crystallized biphosphate of soda	1	140	100.00	100.00

δ . *Ammoniophosphate of Soda.* $\text{NaO}, \text{NH}_4\text{O}, \text{HO}, \text{cPO}_5 + 8\text{HO}$. This salt exists in human urine, whence it was procured by the early chemists under the names of *microcosmic* and *fusible salt*. It may be formed by dissolving in water 5 parts of crystallized rhombic phosphate of soda with 2 of crystallized phosphate of ammonia, and evaporating; or, according to Graham, by heating together 6 or 7 parts of crystallized phosphate of soda, and 2 of water, till the whole is liquid, and then adding 1 part of powdered sal-ammoniac; chloride of sodium separates, and the solution, filtered and concentrated, affords the double phosphate in prismatic crystals; it is purified by a second crystallization. It forms transparent prisms of a

saline and cooling taste, very soluble, fusible, and which effloresce and lose ammonia in a dry atmosphere: they are easily soluble in water, and the solution gives off ammonia when heated. When slightly heated, they part with 8HO; at a red heat the remainder of the water and the ammonia are evolved, and the salt is converted into *metaphosphate of soda*, which is very fusible. "It will be observed," says Professor Graham, "that the three atoms of base in this phosphate are all different, namely, water, oxide of ammonium, and soda. This salt I believe proved the key to the constitution of the bibasic and tribasic organic acids, by supplying the canon founded upon it by myself, that bases of the same family may exist together in the salts of such acids, but not in ordinary double salts." The components of the crystallized salt are

						Riffault.
Soda.....	1	...	32	...	15.16	14.88
Ammonia	1	...	17	...	8.06	9.00
Phosphoric acid	1	...	72	...	34.12	34.49
Water	10	...	90	...	42.66	41.63
<hr/>						
Crystallized ammoniophosphate of soda	1		211		100.00	100.00

2. *Bibasic Phosphates. Pyrophosphates.* There are two phosphates of soda belonging to this class, commonly called the *pyrophosphate* and *bipyrophosphate*.

a. Pyrophosphate of Soda. $2\text{NaO},6\text{PO}_5+10\text{HO}$, is obtained by heating the common phosphate to redness, when it loses its basic water and water of crystallization, and becomes *anhydrous pyrophosphate* = $2\text{NaO},6\text{PO}_5$. Dissolved in hot water this anhydrous salt yields permanent prismatic crystals on cooling, containing 10 atoms of water: these crystals are less soluble than those of the common phosphate, and their solution precipitates nitrate of silver, *white*, (CLARK. *Ed. Journ. Sc.*, VII., 298,) and has an alkaline reaction. All the insoluble pyrophosphates, including that of silver, are soluble to a certain extent in the solution of pyrophosphate of soda. The pyrophosphates of ammonia and of potassa exist in solution, but when they crystallize, they pass into tribasic salts. Pyrophosphate of soda, anhydrous, and crystallized, is composed as follows :

					Clark.					
Soda	2	64	47.05	Soda	2	64	28.31	} 59.28		
Phosphoric acid	1	72	52.95	Phosphoric acid ...	1	72	31.86			
				Water	10	90	39.83		40.72	
<hr/>										
Anhydrous pyrophos- phate of soda	}	1	136	100.00	Crystallized pyro- phosphate of soda	}	1	226	100.00	100.00

β. Bipyrophosphate of Soda. $\text{NaO},\text{HO},6\text{PO}_5$. This salt is formed by the application of a graduated heat to the biphosphate of soda; its solution has an acid reaction, and does not crystallize. It throws down white pyrophosphate of silver from nitrate of silver. It consists of

						Graham.
Soda	1	...	32	...	28·3	} ... 91·98
Phosphoric acid	1	...	72	...	63·8	
Water	1	...	9	...	7·9	
<hr/>						
Bipyrophosphate of soda	1		113		100·0	100·00

3. *Monobasic Phosphate. Metaphosphate of Soda.* NaO, aPO_5 . When any of the preceding phosphates which contain only 1 equivalent of fixed base (soda) are heated to redness, they afford *metaphosphate*: when bipyrophosphate is used, the properties of the resulting salt vary with the temperature to which it has been subjected; thus if heated to 500° , it becomes *neutral*, but still retains the characters of a pyrophosphate. At a temperature somewhat higher, but below redness, it becomes very difficultly soluble, and only feebly acid: when evaporated, this solution does not give crystals, but dries into a transparent pellicle like gum, which retains at the temperature of the air somewhat more than a single equivalent of water. Added to neutral and not very dilute solutions of earthy and metallic salts, metaphosphate of soda throws down insoluble hydrated metaphosphates, of which the physical condition is remarkable; they are all soft solid or semifluid bodies, the metaphosphate of lime having the degree of fluidity of Venice turpentine. Metaphosphate of soda consists of

Soda	1	32	31.37
Phosphoric acid.....	1	72	68.63
<hr/>					
Anhydrous metaphosphate of soda	1		102		100.00

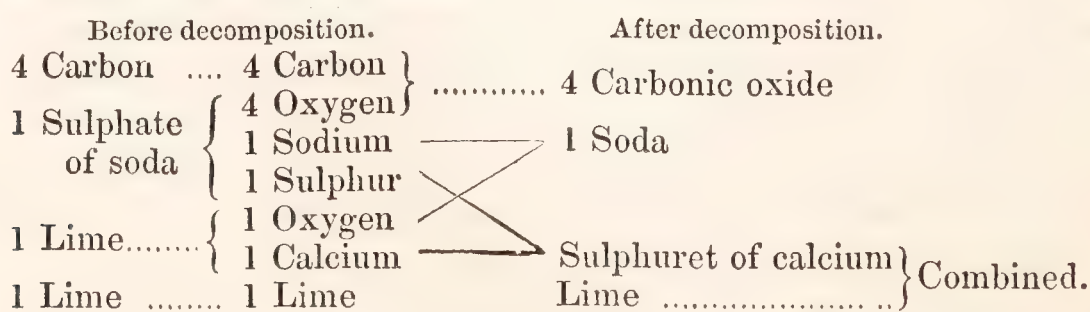
CARBONATE OF SODA. NaO, CO_2 . This important salt was formerly obtained by the combustion of certain marine plants, the ashes of which afforded by lixiviation the impure alkali called *soda*. Two kinds of rough soda were known in the market, *barilla* and *kelp*; besides which, some *native carbonate of soda* was also imported from Egypt. *Barilla* is the semifused ash of the *salsola soda*, which was cultivated upon the Mediterranean shore of Spain, in the vicinity of Alicant. (*Ann. de Chimie*, XLIX. 267.) *Varec* is the impure carbonate made in Brittany, and *Blanquette* that of Aigue-mortes and Frontignan. Kelp consists of the ashes of sea-weeds, collected upon many of the rocky coasts of Britain, and burned in kilns, or merely in excavations made in the ground, and surrounded by stones. It seldom contains more than 5 *per cent.* of carbonated alkali, and about 24 tons of sea-weed are required to produce 1 ton of kelp. The best produce is from the hardest *fuci*, such as the *serratus*, *digitatus*, *nodosus*, and *vesiculosus*. (MACCULLOCH'S *Western Islands*, vol. i. p. 122.) The rough alkali, contaminated by chlorides of potassium and sodium, and other impurities, was to a certain extent purified by dissolving it in a small portion of water, filtrating the solution, and evaporating it at a low heat: but kelp is now only important as a source of iodine (p. 286.) At present the British market is supplied with carbonate of soda obtained by the decomposition of sulphate of soda: it is manufactured to an enormous extent*, at a very cheap rate, and of extreme purity; in many of the arts, soda has accordingly been substituted for potash. Small quantities of carbonate of soda are often found in an efflorescent form, upon walls containing lime and common salt: it also

* Professor Graham states, on the authority of Mr. Muspratt, of Liverpool, that in 1838, 50,000 tons of soda-ash, and 20,000 tons of crystallized carbonate of soda, were made in England by the decomposition of common salt by sulphuric acid, and that the manufacture is greatly on the increase. At present (1846), the produce is probably nearly doubled and may be said to be still on the increase.

occurs in some mineral waters, and in the water of the deep wells in and about London, to which it communicates a peculiar softness. A considerable quantity of carbonate of soda is consumed in the laundry, for it is very detergent, and saves soap.

The following is an outline of the process by which carbonate of soda is now prepared. (GRAHAM, *Elements of Chemistry*. URE'S *Dictionary of Arts*. DUMAS, *Chimie app. aux Arts*.) 1. Sulphate of soda is prepared by the mutual action of equal weights of common salt and sulphuric acid diluted to the density 1.600: these are mixed in the chamber of a reverberating furnace, and the disengaged hydrochloric acid suffered to escape by the chimney, or in some cases condensed, and applied to other manufactures, such as bleaching salts, sal-ammoniac, &c. 2. The sulphate of soda is ground up with an equal weight of chalk and half its weight of powdered coal, and this mixture is fused in a reverberating furnace, well stirred, and then raked out into an iron trough where it cools and solidifies. In this state it is called *ball-soda*, or *British barilla*, and contains about 22 *per cent.* of alkali. 3. This is then broken up, placed in vats, and covered with warm water; in six hours the liquor is drawn off, and the residue repeatedly washed till all soluble matters are extracted: the different liquors are then mixed and evaporated to dryness, by which a carbonate of soda is obtained, mixed with a little caustic soda and sulphuret of sodium. 4. This is further purified by mixing it with one-fourth its weight of sawdust, and exposing the mixture to a dull red heat, by which the sulphur is expelled and the caustic soda converted into carbonate. In this state it contains about 50 *per cent.* of alkali. 5. If crystallized carbonate of soda is required, this dry salt is dissolved in water, and when the solution has become clear, it is poured off, evaporated till a pellicle forms upon the surface, and then run into shallow iron vessels where it crystallizes. 6. The mother-liquors are boiled down to dryness, and yield a less pure salt, containing about 30 *per cent.* of alkali, which is used for soap and glass-making.

In this process the sulphate of soda becomes sulphuret of sodium in consequence of the calcination with coal, and this sulphuret is converted into carbonate by the action of the chalk, sulphuret of calcium being also formed. Graham observes that this sulphuretted calcium would destroy the carbonate of soda if dissolved along with it in the lixiviation of the ball soda, but that being in combination with the lime, as an oxysulphuret of calcium, this does not happen; hence the necessity of excess of lime: he gives the following diagram in illustration of the process, assuming that charcoal is used instead of coal, and lime instead of carbonate of lime: the numbers denote equivalents.



The soda acquires carbonic acid, either from the carbonate of lime, or from the fuel. The insoluble oxysulphuret of calcium in this process is known as *soda-waste*. It has, hitherto, says Graham, "been not merely value-

less but troublesome to the manufacturer: at present an attempt is making to turn it to account as a source of sulphur."

R. Phillips has suggested the use of sulphate of iron obtained by the oxidation of iron pyrites, as a substitute for the sulphuric acid in the above process, to convert the chloride of sodium into sulphate of soda; in this case sulphate of soda, oxide of iron, and a volatile chloride of iron, are the results; or the salts may be dissolved and the solution exposed to a low temperature, when sulphate of soda crystallizes and chloride of iron remains dissolved. Sulphate of magnesia has also been substituted in this process, for sulphate of iron.

Another mode of producing carbonate of soda, consists in the mutual decomposition which ensues when carbonate of ammonia and chloride of sodium are made to re-act upon each other in the humid way: the following is an outline of this process; it has been patented by Messrs. Dyer and Hemming: "Mix common salt with an equivalent proportion of sesquicarbonate of ammonia, and as much water as will dissolve the salt. Keep the ingredients in constant agitation for several hours; the result is a thick magma. Filter the liquid from the solid, and afterwards submit the solid to great pressure by an hydraulic press. The solid cake, which is chiefly bicarbonate of soda, is then heated in an iron retort till all the moisture, and one equivalent of carbonic acid, are expelled; it is now good soda-ash. The retorts are provided with pipes, communicating with a tank, in which the volatilized carbonate of ammonia is saved. The filtered and expressed liquors (which chiefly contain sal-ammoniac) are distilled with lime, and yield a solution of caustic ammonia. This is added to an equivalent proportion of common salt and agitated for several hours, during which a current of carbonic acid, obtained from ignited coke mixed with chalk, is forced through the mixture. The vats in which this operation is performed are rendered airtight, and the gas passes from one to another, and finally into a waste tub containing salt and water; the arrangement of the mixing vats being similar to that of a series of Woulfe's bottles. The carbonic acid converts the caustic ammonia into carbonate, which decomposes the common salt as it is formed: the results are treated as before described. The chalk from which the carbonic acid is obtained, furnishes the lime for the distilled liquors. The ammonia is chiefly obtained by distilling the ammoniacal liquor of coal gas with lime, and redistilling with a little more lime. By this mode a *very strong* solution of caustic ammonia is procured, somewhat contaminated with sulphuretted hydrogen: this, however, is displaced by carbonic acid. It may be necessary to observe that the carbonic acid is passed through two waters to wash and cool it, and as it is indispensable that the mixtures should be kept *cool*, the water in the coolers is kept about one foot deeper than the column in the mixing vats, so that the gas enters under pressure, and by expanding cools the mixtures. When there is abundance of liquid ammonia, the filtered and expressed liquors may be distilled *per se*, by which any free, or carbonated ammonia is separated; the residue is a solution of common salt and sal-ammoniac. At a boiling heat the common salt, being much less soluble than the sal-ammoniac, is taken out in the solid state and used again. The solution of sal-ammoniac is boiled to dryness, and, resublimed in the usual way, furnishes an excellent article."

A process has also been patented for decomposing common salt at high temperatures by the joint action of silica and water: under these circumstances hydrochloric acid is evolved, and a silicate of soda is formed, which is afterwards converted into a subsilicate, and so rendered soluble in water by fusion with a due addition of carbonate of soda; this solution is decomposed by a current of carbonic acid; gelatinous silica is thrown down, and a carbonate of soda remains in solution. (*Chem. Gaz.*, June, 1843.)

The primitive crystalline form of the common, or decahydrous carbonate of soda is an oblique rhombic prism, the modifications of which have been described by Brook. (*Ann. of Phil.*, N. S., vi. 287.) Its usual form is a rhombic octohedron, the acute angles of which are truncated. Its sp. gr. is 1.42. It is soluble in twice its weight of water at 60°, and in less than its own weight at 212°. “The strongest solution that can be preserved at the temperature of the atmosphere has the specific gravity 1.26; but even this is liable to partial crystallization.” (HENRY.) Its taste is strongly alkaline, and it greens vegetable blues. It fuses very readily in its water of crystallization, and on pouring off the fused salt, a portion of monohydrous carbonate remains. The fused salt congeals at about 90°. Exposed to a dry atmosphere, the crystals effloresce, and gradually crumble down into a white powder; at a red heat it loses the whole of its water. When the vapor of a boiling solution of carbonate of soda is introduced into a flame, it gives it a yellow color, in consequence of traces of the salt passing off with the aqueous vapor.

The following table by Tünnermann (*GMELIN, Handbuch*, ii. 82) shows the quantity of anhydrous carbonate of soda contained in solutions of the annexed specific gravities at the temperature of 60°:

Sp. gr.	Per Cent.	Sp. gr.	Per Cent.	Sp. gr.	Per Cent.	Sp. gr.	Per Cent.
1.1816 14.880	1.1308 11.160	1.0847 7.440	1.0410 3.720
1.1748 14.508	1.1261 10.788	1.0802 6.768	1.0368 3.348
1.1698 14.136	1.1214 10.416	1.0757 6.396	1.0327 2.976
1.1648 13.764	1.1167 10.044	1.0713 6.324	1.0286 2.504
1.1598 13.392	1.1120 9.672	1.0669 5.972	1.0245 2.232
1.1549 13.020	1.1074 9.300	1.0625 5.580	1.0204 1.850
1.1500 12.648	1.1028 8.928	1.0578 5.208	1.0163 1.488
1.1452 12.276	1.0982 8.556	1.0537 4.836	1.0121 1.116
1.1404 11.904	1.0937 8.184	1.0494 4.464	1.0081 0.744
1.1356 11.532	1.0892 7.812	1.0452 4.092	1.0040 0.372

Anhydrous carbonate of soda contains,

	Berzelius.		Dalton.		Ure.	
Soda	1 32 59.26 58.75 59.6 59.14
Carbonic acid	1 22 40.74 41.25 40.4 40.86
<hr/>						
Anhydrous carbonate of soda	1	54	100.00	100.00	100.0	100.00

The perfect crystals, as they ordinarily occur, contain

	Bergman.		Klaproth.		V. Rose.	
Soda	1 32 22.22 20 22 24
Carbonic acid	1 22 15.28 16 16 15
Water	10 90 62.50 64 62 61
<hr/>						
Crystals of carbonate of soda....	1	144	100.00	100	100	100

When the crystals are obtained at a temperature between 80° and 90° , they sometimes form large right rectangular prisms, terminated by a four-sided pyramid: these only contain 8 equivalents of water. A saturated solution of carbonate of soda, kept for a long time at 120° , deposited transparent prismatic crystals, harder than the common carbonate, and containing only 1 equivalent of water; and another variety, described by Mohs, contained $1\frac{1}{2}$ of water. Crystals containing 5 and 6 atoms of water have also been described. (GMELIN, *Handbuch*.)

In the analysis of barilla, kelp, and other impure kinds of soda, to ascertain the relative proportion of soda, it may be useful to know that 100 parts of dilute nitric acid, specific gravity 1.36, will saturate 50 parts of dry carbonate of soda, which are equivalent to about 29 of pure soda; or 460 grains of dilute sulphuric acid, specific gravity 1.141, neutralize 100 grains of the dry carbonate. From either of these data, the quantity of real alkali in any sample of the rough salt may be calculated. But the method of ascertaining the proportion of soda, or of carbonate of soda, in these cases, by means of the *alkalimeter*, has already been described. (See *Alkalimetry*, p. 593; GAY LUSSAC and WELTER, *Ann. Ch. et Ph.*, xiii. 212. On the Analysis of *Black ash*, R. PHILLIPS, Jun., *Pharm. Journ.*, iv. 122; and F. P. DULK, *Chem. Gaz.*, Jan. 1846.)

The principal impurities contained in carbonates of soda are detected as follows: 1. *Hyposulphite of soda*. Hydrochloric acid evolves sulphurous acid, and sulphur gradually falls. 2. *Sulphate of soda*. A precipitate by chloride of barium when the solution is supersaturated by hydrochloric acid. 3. *Chloride of sodium*. By a precipitate with nitrate of silver in the solution supersaturated by nitric acid. 4. *Ferrocyanides* by blue with protosulphate of iron and excess of hydrochloric acid. 5. *Salts of potassa*, by chloride of platinum, or tartaric acid (p. 603). 6. *Lime* by oxalic acid. Carbonate of lime is rendered soluble to a certain extent by carbonate of soda, and is retained after recrystallization: such a solution cooled to 32° , deposits a white crystalline powder composed of the two carbonates. (L. GMELIN.)

CHLORINATED CARBONATE OF SODA. It has above been stated that when excess of chlorine is passed into a solution of carbonate of potassa or of soda, carbonic acid is expelled and chlorides and chlorates formed; by proper management, however, chlorine may be combined with a solution of carbonate of soda, and the resulting combination has, from the uses made of it, and the name of its inventor, been termed *Labarraque's disinfecting liquid*. It is obtained as follows: 2800 grains of crystallized carbonate of soda are dissolved in 1.28 pints of water, and being put into a Woulfe's apparatus, the chlorine slowly evolved from a mixture of 967 grains of salt with 750 grains of black oxide of manganese, and 967 grains of sulphuric acid, previously diluted with 750 grains of water, is carefully passed into it. No carbonic acid is evolved, and a pale yellow liquid is the result; its taste is sharp, saline, and astringent, and it at first reddens, and then bleaches turmeric paper. It is but little changed by a boiling heat, and gives out no chlorine. By *careful* evaporation, it furnishes crystals which produce the original liquid when redissolved; but exposed to the air, and suffered to evaporate spontaneously, the chlorine escapes, and crystals of carbonate of soda are

obtained. (FARADAY, *Quarterly Journal*, N. S., vol. ii. p. 84. See also *Chloride of Potassa*, p. 563.)

BICARBONATE OF SODA, $\text{NaO}, 2\text{CO}_2, \text{HO}$, or $\text{NaO}, \text{CO}_2 + \text{HO}, \text{CO}_2$, is formed by passing carbonic acid through a strong solution of the carbonate; a granular or crystalline powder is deposited, which, when carefully dried at common temperatures, consists of 1 atom of bicarbonate of soda, with, according to some 1 atom, according to others 2 atoms, of water. Both combinations may probably be formed.

This salt (as the bicarbonate of potassa, p. 597) may be obtained by treating the carbonate by carbonate of ammonia; pure ammonia is evolved and bicarbonate formed. Bicarbonate of soda may also be obtained by condensing carbonic acid upon crystals of the carbonate; a portion of the water of the latter salt separates, and when the gas ceases to be absorbed, it is found converted into a porous and friable bicarbonate, which must be carefully dried at a low temperature, otherwise it loses a portion of its carbonic acid, and becomes a sesquicarbonate. The salt directed for pharmaceutical use is represented by Phillips as a sesquicarbonate, obtained by drying the bicarbonate "by a gentle heat." (*London Pharmacopœia*.) According to Graham, the bicarbonate of commerce generally contains 40 *per cent.* of soda, owing to the presence of neutral carbonate, in the state of protohydrate, which last salt may be separated by a small quantity of water. The production of bicarbonate of soda by the mutual action of carbonate of ammonia and chloride of sodium has been mentioned above (p. 623).

In the manufacture of this bicarbonate for the purpose of commerce, 160lbs. of crystallized carbonate may be dissolved in 13 gallons of water, and carbonic acid thrown into the solution in a proper apparatus. The bicarbonate falls as it forms to the amount of about 50lbs., and being separated from the solution may be conveniently dried by pressure in an hydraulic press. A fresh portion of carbonate is dissolved in the mother-liquor, and the operation repeated as before.

Bicarbonate of soda has a slight alkaline taste, but its solution has no alkaline reaction upon turmeric; it renders brazil-wood paper blue, and of course restores the blue color of reddened litmus; it also greens violet juice. It is much less soluble in water than the carbonate, requiring, according to Berthollet 8, according to Rose 13, of cold water. According to Poggiale, (BERZELIUS, *Lehrbuch*,) 100 parts of water at 32° dissolve 8.95 of bicarbonate of soda; at 50° , 13.04 parts; at 68° , 11.15 parts; at 86° , 12.24 parts; at 122° , 14.45 parts; and at 158° , 16.69 parts; at higher temperatures the salt begins to lose carbonic acid. The crystals of this bicarbonate are four-sided tables, or, according to Thomson, oblique rectangular prisms. It loses carbonic acid if moistened and left in the vacuum of an air-pump, and the gas is also evolved when 1 part of the salt is boiled with 4 of water. In these cases, the salt was supposed to be converted into a *sesquicarbonate* (*Quarterly Journal*, xv. 383), but, according to Rose, 1 atom of carbonic acid is evolved. At a red-heat bicarbonate of soda loses its water, and half its acid, and becomes converted into dry carbonate of soda. When long exposed to damp air, it is converted, after some months, into pentahydrated monocarbonate. $\text{NaO}, \text{CO}_2, 5\text{HO}$. (BERZELIUS.)

The components of bicarbonate of soda, in its driest state, are

					R. Smith.	Stromeyer.	Berzelius.	Schindler.
Soda.....	1	...	32	...	37·6	...	37·06	} ... 89·26 ... 89·31
Carbonic	2	...	44	...	52·6	...	52·20	
Water	1	...	9	...	9·8	...	10·74	... 10·74 ... 10·69
<hr/>								
Bicarbonate of soda	1		85		100·0		100·00	100·00 100·00

SESQUICARBONATE OF SODA. $2\text{NaO}, 3\text{CO}_2$. A carbonate of soda occurs *native* in the Soda Lakes of Hungary; also in Africa, in the province of Gahena, near Fezzan, where the natives call it *Trona*: it is in hard striated crystalline masses, not altered by exposure to air: indeed the walls of Cassar, a fort now in ruins, are said to have been built of it. A productive soda lake also exists in South America, in Maracaybo, one of the provinces of Venezuela. Klaproth and Phillips have shown that these carbonates are intermediate between the carbonate and bicarbonate. *Beiträge*, iii. 98, and *Quart. Journ.*, vii. 298.)

A crystallized sesquicarbonate is deposited when a solution of the bicarbonate is boiled and then cooled; or when it is evaporated in vacuo. The conditions under which this sesquicarbonate is formed have been examined by Hermann (*Chem. Gaz.*, Jan. 1843): it does not apparently originate from aqueous solution, for in that state it is decomposed into monocarbonate and bicarbonate, which crystallize separately; but it may be formed by fusing single atoms of bicarbonate and crystallized carbonate in their water of crystallization, or by exposing bicarbonate to a heat not exceeding 482° , and leaving the mass exposed to humid air, when in a few weeks it assumes the characters of crystallized sesquicarbonate or trona. Hermann's and Winckler's analyses lead to the formula $2\text{NaO}, 3\text{CO}_2, 3\text{HO}$ for the artificial salt, whereas the analyses of African trona and of African urao, by Klaproth and Boussingault, and of the artificial salt by Phillips, give 4HO ; there are therefore probably two states of hydration, namely,

					Hermann.	Winckler.
Soda	2	64	40·76	40·00	41·13	
Carbonic acid ...	3	66	42·04	43·06	43·31	
Water	3	27	17·20	16·94	15·56	
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	
	1	157	100·00	100·00	100·00	

						Boussingault.		Klaproth.		R. Phillips.
						<i>Urao.</i>		<i>Trona.</i>		
Soda	2	...	64	...	38·5	...	41·22	...	37·0	} ... 78·2
Carbonic acid ...	3	...	66	...	39·8	...	39·00	...	38·0	
Water	4	...	36	...	21·7	...	18·80	...	22·5	... 21·8
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>	<hr/>
	1		166		100·0		100·00		100·0	100·0

CARBONATE OF SODA AND POTASSA, $\text{NaO}, \text{CO}_2 + \text{KO}, \text{CO}_2$, is obtained by fusing the salts in single atomic equivalents: the double salt is much more fusible than its components, and is therefore conveniently used in many cases of mineral analysis by fusion. When dissolved in water the component carbonates separate. (MITSCHERLICH, *Poggend.*, xiv. 109.) This double salt was recognized by Dubrunfaut in the incinerated residue of fermented beet-root melasses: it formed oblique rectangular prisms, which, on exposure to air, absorbed carbonic acid, forming porous

bicarbonate of soda and deliquescent carbonate of potassa. The crystals were $= \text{NaO}, \text{KO}, 2\text{CO}_2, 12\text{HO}$. Another double carbonate $= 2\text{NaO}, \text{CO}_2 + \text{KO}, \text{CO}_2 + 18\text{HO}$, has been described by Marguerite. (*Journ. de Pharm.*)

CYANIDE OF SODIUM. NaCy . Sodium and cyanogen act with the same phenomena as potassium and cyanogen, and the resulting cyanides much resemble each other. Cyanide of sodium is insoluble in alcohol, readily soluble in water, and difficultly crystallized.

SULPHOCYANIDE OF SODIUM, NaCsy , is formed as the potassa salt. It may be obtained from a concentrated hot solution in deliquescent rhombic crystals, which are anhydrous, and soluble in alcohol.

MELLONIDE OF SODIUM, NaMe , is best obtained by the decomposition of mellonide of barium by carbonate of soda: it forms white silky acicular hydrated crystals, soluble in water, but not in alcohol. (BERZELIUS.)

BORATE OF SODA. BORAX. BIBORATE OF SODA. $\text{NaO}, 2\text{BO}_3$. This salt, which has been very long known, is imported from India, in an impure state, under the name of *Tincal*, *Pounxa*, or *Chrysocolla*; when purified, it is called *Borax*. It is also manufactured by combining soda with native boracic acid imported from the South of Italy. This process, as well as the methods of refining Indian and Chinese borax, are described by Dumas (*Chim. app. aux Arts*, ii.) and by Pereira (*Mat. Med.*) Common borax crystallizes in transparent prisms, slightly efflorescent. Its taste is cooling and alkaline: it has an alkaline reaction upon turmeric. It is soluble in 12 parts of cold and 2 of boiling water. When heated it loses water of crystallization, and becomes a porous friable mass, called *calcined borax*. At a red-heat it runs into a transparent glass, which, by exposure to air, becomes opaque and pulverulent upon the surface. Its specific gravity in this state is 2.36.

Anhydrous borax consists of

						Arfwedson.	Soubeiran.
Soda	1	...	32	...	31.37	...	31.4
Boracic acid	2	...	70	...	68.63	...	68.6
<hr/>					<hr/>		<hr/>
Anhydrous biborate of soda	1		102		100.00		100.0
							100.000

and the common crystallized borax, $= \text{NaO}, 2\text{BO}_3, 10\text{HO}$, of

						Kirwan.	Berzelius.	L. Gmelin.
Soda.....	1	...	32	...	16.66	...	17	...
Boracic acid	2	...	70	...	36.45	...	34	...
Water	10	...	90	...	46.89	...	49	...
<hr/>					<hr/>		<hr/>	<hr/>
Prismatic biborate of soda	1		192		100.00		100	
							100.00	
								100.0

Sulphuric acid decomposes this salt, producing sulphate of soda and boracic acid (p. 526). It is also decomposed by nitric and hydrochloric acids, and by the greater number of the vegetable acids. It has a place in the *Pharmacopœia*. It is often used as a blow-pipe flux, vitrifying the greater number of the metallic oxides, and forming beads of different colors: violet with manganese; green with iron, chromium, and copper;

blue with cobalt; and slightly yellow with some of the colorless oxides. This property of borax renders it also an useful ingredient in the pastes which are manufactured under the name of *artificial gems*. In the reduction of the metals by charcoal, borax is often useful as forming a medium through which the globules fall and collect into a button, being at the same time protected from the air. At the potteries it is used in the glazes applied to the better kinds of earthenware, and to porcelain. Alone, or mixed with phosphate of ammonia or soda, borax is employed to render muslin and other articles of dress, as also paper, wood, and other materials, to a certain extent incombustible; this it does by covering them with a vitrifiable glaze by which the access of air is prevented. (See also p. 426.) Borax is also used in the process of *soldering*; when, for instance, two surfaces of copper are to be soldered together they are scraped or rubbed clean, sprinkled with a mixture of powdered borax and solder-filings, and heated till the solder fuses so as to alloy with the copper and make a perfect joint: the borax not only prevents the contact of air, and consequent oxidation of the metals, but dissolves any oxide accidentally formed, and so retains the surfaces in that perfectly clean state which is requisite for their union. An aqueous solution of borax dissolves several of the resins, and some of these solutions, especially that of lac, form good vehicles for coloring materials.

OCTOHEDRAL BORAX. $\text{NaO}, 2\text{BO}_3, 5\text{HO}$. This salt, discovered by Payen, contains 5 instead of 10 atoms of water: it is obtained by dissolving common borax in boiling water till the solution has a specific gravity 1.26; it is then allowed to cool slowly, and between the temperatures of 174° and 145° it deposits octohedral crystals; below that temperature, the ordinary prismatic crystals are formed. Octohedral borax is harder than the prismatic; its specific gravity is 1.815; it has a brilliant conchoidal fracture, and is preferred for brazing and soldering.

						Payen.
Soda	1	...	32	...	21.8	} ... 69.36
Boracic	2	...	70	...	47.7	
Water	5	...	45	...	30.5	
<hr/>						<hr/>
Octohedral borax	1		147		100.0	100.00

BOROFLUORIDE OF SODIUM, NaF, BF_3 , is obtained by combining fluoride of sodium with fluoboric acid: it forms prismatic crystals of a bitter and sour taste, easily soluble in water, fusible and anhydrous. (BERZELIUS.) By dissolving 3 atoms of fluoride of sodium and 1 of boracic acid in boiling water, rhomboidal crystals are formed on cooling, $= 3\text{NaF}, \text{BO}_3, \text{HO}$.

SODIUM AND POTASSIUM form an *alloy*, which, if composed of 1 part of potassium and 3 of sodium, remains fluid at 32° . Equal parts of the metals form a brittle crystallizable alloy.

THE SALTS OF SODIUM are soluble in water, and generally more so than the corresponding salts of potassa. They do not afford any precipitate either with perchloric or tartaric acids, inasmuch as the perchlorate and bitartrate of soda are very soluble: nor are they affected by the addition

of chloride of platinum. With sulphate of alumina they produce soda alum, which, however, is much more soluble and less easily crystallizable than potassa alum, so that soda cannot in that way be separated from its solutions. According to Wackenroder (*Chem. Gaz.*, Nov. 1843), a solution of antimoniate of potassa gives a precipitate with soda salts, but none with those of potassa; this test, however, is not sufficiently characteristic to be relied on. (See *Antimony*.) Before the blow-pipe, potash and soda salts may be distinguished by the purple tint communicated to the flame by the former, and the characteristic yellow of the latter. Dip a clean platinum wire into the solution of the salt to be tested; dry it over a flame of pure alcohol burning in a small saucer; then put the wire into the blue part of the flame: if potassa, a rich purple or lilac tint is given; if soda, a bright yellow; these appearances are best seen in a dark corner: the yellow color given by soda is more decided than the purple by potassa, so that smaller quantities of the former may be thus recognized. (CLARK.) When potassa or a salt of potassa is added to a globule of fused borax and oxide of nickel before the blow-pipe, they communicate to it a blue color, which is not the case with soda or the salts of soda. But the best distinction between these two alkalis is found in the perfectly distinctive characters of their respective sulphates, carbonates, and nitrates, and more especially in the prismatic, efflorescent, fusible, and soluble character of the sulphate soda, compared with the corresponding salt of potassa.

§ III. LITHIUM. L. 7.

IN the analysis of a mineral found in the mines of Utö, in Sweden, called *petalite*, M. Arfwedson, in 1817, discovered between 5 and 6 *per cent.* of an alkaline substance, which was at first supposed to be soda; but, finding that it required for its neutralization a much larger quantity of acid than soda, he was led to doubt its identity with that alkali, and the further prosecution of his inquiries demonstrated that it possessed peculiar properties. The mineral called *triphane*, or *spodumene*, also from Utö, and found also at Killiney, near Dublin, affords the same substance to the amount of nearly 9 *per cent.*, and it exists in *lepidolite*, in some varieties of *mica*, in *green tourmaline*, and according to Berzelius, in the waters of Carlsbad in Bohemia, of Kissingen, and of some other mineral springs: the term *lithia*, deduced from its lapideous original (*λίθιος*, *lapideus*), has been applied to it.

The following is Arfwedson's mode of obtaining lithia from the *petalite*: Reduce the mineral to a fine powder, and fuse it with about half its weight of potassa; dissolve the fused mass in hydrochloric acid, filter, and evaporate to dryness; digest the residue in alcohol; the only substance present, soluble in that liquid, is the *chloride of lithium*, which is taken up, and by a second solution and evaporation is obtained pure. It may be decomposed by digesting carbonate of silver in its aqueous solution, by which a carbonate of lithia is formed, decomposable by lime, in the way of the other alkaline carbonates.

Berzelius separates lithia from *spodumene* or from *petalite* as follows; One part of the mineral is reduced to a fine powder with about two parts

of fluor-spar; this mixture is made into a thin paste with sulphuric acid, and heated in a silver crucible as long as acid vapors are given off, and ultimately to redness nearly; the dry mass is then digested in water, filtered, boiled with caustic ammonia to precipitate any alumina that may be present, filtered again, and evaporated to dryness: the dry mass, after having been heated to redness, to expel sulphate of ammonia, is pure *sulphate of lithia*, from the concentrated solution of which the lithia may be thrown down in the state of *carbonate*, by carbonate of ammonia.

Dumas directs as follows: Reduce the mineral containing lithia to fine powder, mix it with four parts of carbonate or nitrate of baryta, and expose it to a high heat in a platinum crucible for an hour and a half: a compact white mass is obtained, which is partially soluble in dilute hydrochloric acid; evaporate this solution till the chlorides remain dry: the silica may be separated by washing the residue in boiling water, filtering the liquor, and washing the filter; the silica remains upon the filter. The filtered liquor contains the chlorides of lithium, aluminum, barium, and iron; add to it a sufficiency of sulphuric acid to precipitate the barium and decompose the chlorides; saturate the excess of acid by ammonia, and add carbonate of ammonia to the diluted neutralized solution, which precipitates alumina and oxide of iron. One filtration is sufficient to separate these precipitates, and the liquor then contains sulphate and hydrochlorate of ammonia, and sulphate of lithia; evaporate it to dryness, drive off the volatile salts, and pure sulphate of lithia remains. Dissolve the sulphate of lithia in water, and add a sufficiency of baryta water to precipitate the sulphuric acid; the lithia remains in solution and may be obtained by evaporating the filtered liquor to dryness. Or the sulphate of lithia may be decomposed by acetate of baryta; filter and evaporate the solution of acetate of lithia to dryness, heat the residue in a platinum crucible, and fused carbonate of lithia remains: powder and dissolve it in hot water, and boil it with hydrate of lime, by which it is decomposed, and on filtering, carbonate of lime remains, and a solution of pure lithia is obtained. A number of other processes have been devised for the separation of lithia, abstracts of which are given by Gmelin. (*Handbuch.*)

PROTOXIDE OF LITHIUM. LITHIA, LO , is a white caustic substance, and when submitted, in the state of hydrate, to the action of the Voltaic pile, it is decomposed with the same phenomena as potassa and soda; a white and highly combustible metal is separated at the negative pole. The properties of this metal have not been examined.

Hydrate of lithia is less soluble in water than potassa or soda; its solution tastes acrid like the other fixed alkalis, and exhibits a powerful alkaline reaction upon test-papers. It is sparingly soluble in alcohol. It does not deliquesce by exposure, but absorbs carbonic acid and becomes opaque: it affords no precipitate with chloride of platinum, in which it differs from potassa, but resembles soda. It attacks platinum in its pure and carbonated state, and hence must be fused in a silver crucible. It probably forms a peroxide. When its salts are heated on platinum before the blow-pipe, they tinge the flame red. Its principal distinctive characters are found in its salts.

Direct experiments upon the composition of lithia are yet wanting.

By calculation from the composition of the sulphate, as analyzed by Vauquelin, it would appear to contain about 55·2 lithium + 44·8 oxygen; by other experimentalists, nearly the same results have been admitted; so that the number 10 has been generally assumed as the equivalent of lithium; but from the analysis of some of its salts by Hermann, of Moscow (*Poggend.*, xv.), as also by C. Gmelin, it appears that its atomic weight lies between 6 and 7: I shall employ the latter number. (6·4 GMELIN. 6 HERMANN.)

Lithium.....	1	7	46·7
Oxygen	1	8	53·3
<hr/>					
Lithia.....	1		15		100·0

CHLORIDE OF LITHIUM. This compound is obtained by dissolving lithia or its carbonate in hydrochloric acid, evaporating the solution to dryness, and fusing it out of the contact of air: it is a white semi-transparent substance. It differs from the chlorides of potassium and sodium, in being extremely deliquescent; in being soluble in absolute alcohol; in being decomposed when strongly heated in the open air, when it loses chlorine, absorbs oxygen, and becomes highly alkaline; in being very difficultly crystallizable in cubes; and in tinging the flame of alcohol of a red color. It consists of

						Hermann.	Gmelin.		
Lithium.....	1	...	7	...	16·28	...	14·66	...	18·43
Chlorine	1	...	36	...	83·72	...	85·34	...	81·57
<hr/>									
Chloride of lithium	1		43		100·00		100·00		100·00

When chloride of lithium deliquesces in the air, the solution gradually yields four-sided prismatic crystals: when touched, they become opaque, and crumble: they contain 46 *per cent.* of water = $\text{LiCl} + 4\text{HO}$.

CHLORATE OF LITHIA. $\text{LO}, \text{ClO}_5, \text{HO}$. Chloric acid saturated with carbonate of lithia and evaporated in vacuo over sulphuric acid yields a radiated crystalline mass, deliquescent, soluble in alcohol, and containing 14·59 *per cent.* of lithia. (WAECHTER.)

LITHIUM AND IODINE. The action of *iodine* on lithium has not been investigated, nor has the iodide of lithium been obtained by the action of hydriodic acid upon lithia or its carbonate. The aqueous solution of *iodate of lithia* gives an anhydrous salt on evaporation, soluble in 2 parts of cold, and in not much less boiling water. (RAMMELSBERG, *Poggend.*, xlv. 555.)

LITHIUM AND BROMINE. The aqueous solution of *bromate of lithia* evaporated in vacuo over oil of vitriol yields very deliquescent acicular crystals. (*Poggend.*, lv. 63.)

FLUORIDE OF LITHIUM is very difficultly soluble. Its solution deposits small opaque crystals. (BERZELIUS.)

NITRATE OF LITHIA. LO, NO_5 , is a very soluble and extremely deliquescent salt, fusible and decomposed by heat: its taste is cooling; it crystallizes in rhombic and acicular prisms; and is soluble in alcohol.

SULPHURET OF LITHIUM. The action of sulphur on lithium and lithia appears analogous to its action on potassium and potassa, but the compounds have not been precisely examined.

SULPHATE OF LITHIA. LO,SO_3 . The anhydrous salt is white and difficultly fusible, unless sulphate of lime be present, when it fuses below redness; its taste is saline, but not bitter. It consists of

						C. Gmelin. Hermann.			
Lithia.....	1	15	27.27	27.94	26
Sulphuric acid	1	40	72.73	72.06	74
<hr/>						<hr/>		<hr/>	
Anhydrous sulphate of lithia	1		55		100.00		100.00		100

The crystals of sulphate of lithia are rhombic prisms and plates, slightly efflorescent; they decrepitate when heated, and lose water without fusing; they are easily soluble in water and alcohol. They consist of

						Hagen.	Arfwedson.	Hermann.	
Lithia.....	1	...	15	...	23.44	...	22.61	...	27.3
Sulphuric acid	1	...	40	...	62.50	...	62.42	...	58.4
Water	1	...	9	...	14.06	...	14.97	...	14.3
<hr/>						<hr/>		<hr/>	
Crystallized sulphate of lithia	1		64		100.00		100.00		100.0

BISULPHATE OF LITHIA. $\text{LO},2\text{SO}_3$, has been described as crystallizing in hexangular tables; but Berzelius denies that it is a distant salt: he, however, admits that sulphate of lithia forms larger crystals when the solution contains excess of acid.

PHOSPHATE OF LITHIA has been examined by Gmelin: it may be obtained by adding phosphoric acid to sulphate of lithia; no precipitate is at first formed, but on adding excess of ammonia, an insoluble *phosphate of lithia* falls. This property enables us to separate lithia from potassa and soda. The phosphate of lithia may be decomposed by dissolving it in acetic acid, and adding acetate of lead: *acetate of lithia* remains in solution.

AMMONIO-PHOSPHATE OF LITHIA falls in crystalline grains, when a mixed solution of a salt of lithia and phosphate of ammonia is evaporated; the phosphate must not be in excess, and the solutions should be concentrated, and the evaporation slow, lest the ammonia escape and the liquid become sour. This salt resembles the ammonio-magnesian phosphate in appearance, and it is fusible and evolves ammonia; but when heated with nitrate of cobalt, it becomes blue, whereas the magnesian salt becomes red. (BERZELIUS.)

PHOSPHATE OF SODA AND LITHIA is obtained when a salt of lithia is mixed with phosphate of soda and evaporated to dryness. The solution at first becomes turbid; but the double salt is chiefly formed during the drying of the mass, which when digested in a little water leaves it in the form of a light white powder. It is insoluble in fluids containing phosphoric salts, very sparingly soluble in cold water, and somewhat more soluble in boiling water. This salt, after exposure to a red heat, contains 15.08 *per cent.* of lithia. It is so sparingly soluble in water that it may

be resorted to for the discovery of small traces of lithia in solutions, which for this purpose must be mixed with carbonate of soda, evaporated to dryness, the residue heated red-hot and redissolved in water, by which all other salts precipitable by phosphoric acid are got rid of; phosphate of soda is then added to the solution, and it is evaporated to perfect dryness; when this residue is acted on by water, the double phosphate remains undissolved. In appearance it resembles phosphate of lime or magnesia, from which it may be distinguished as follows: fused with carbonate of soda upon platinum-foil it is transparent, but becomes turbid on cooling, whereas the earthy salts do not fuse in this way with the alkali; if the fusion be performed on charcoal, the fused double salt is absorbed, but the earthy salts remain upon the charcoal. (BERZELIUS.)

CARBONATE OF LITHIA. LO, CO_2 . When a strong solution of carbonate of ammonia is added to sulphate of lithia, a white precipitate of *carbonate of lithia* is formed. According to Dumas, it is best formed by decomposing sulphate of lithia by acetate of baryta, and calcining the resulting acetate of lithia; the small remaining portions of carbonate of baryta and carbon are removed by digestion in boiling water and filtering; by slow evaporation a crust of very small prismatic crystals of carbonate of lithia separates.

Carbonate of lithia requires at least 100 parts of water at 60° for its solution; (very difficultly soluble, or according to some insoluble, in cold water.) It is insoluble in alcohol. It is fusible, and alkaline; it effervesces with acids; a solution containing only 1-1000th of its weight, acts strongly upon vegetable colors. It is decomposed by lime and baryta. It consists of

					C. Gmelin. Hermann. Schaffgotsch.						
Lithia	1	15	40.54	45.54	39	39.83
Carbonic acid	1	22	59.46	54.46	61	60.17
<hr/>					<hr/>						
Carbonate of lithia	1		37		100.00		100.00		100		100.00

BICARBONATE OF LITHIA. Carbonate of lithia is slightly soluble in water impregnated with carbonic acid. It is said to occur in this state in some mineral waters in Bohemia. By spontaneous evaporation, the carbonate separates in the form of a crystalline crust.

BORATE OF LITHIA much resembles borate of soda: it is alkaline to tests.

CHARACTERS OF THE SALTS OF LITHIA. It appears from the preceding statement, that lithia is distinguished from potassa and soda by its greater saturating power in respect to acids: that is, by its lower equivalent number; and by forming difficultly-soluble salts with phosphoric and carbonic acids. Chloride of lithium is highly deliquescent, and dissolves in strong alcohol, which enables us to separate it from the chlorides of potassium and of sodium. This solution burns with a purplish flame, and the same tint is communicated to the flame of the blow-pipe when any salt of lithia is fused upon a thin slip of platinum-foil; they also corrode that metal, and leave a yellow spot at the point of action. The influence of the presence of soda in this detection of lithia, has been

noticed by Stein. (*Ch. Gaz.*, June, 1844.) Lithia is distinguished from the alkaline earths by forming soluble salts with sulphuric and oxalic acids, and by the alkaline re-action of its carbonate upon vegetable colors. Its salts are not precipitated by ferrocyanide of potassium, nor by infusion of galls, nor by chloride of platinum, nor by caustic potassa: the precipitate, by carbonate of ammonia, being carbonate of lithia, redissolves when the liquid is diluted and boiled.

§ IV. CALCIUM. Ca. 20.

THE existence of *calcium*, as the metallic base of lime, was first demonstrated by Davy in 1808; he found that when moistened lime was rendered electro-negative in contact with mercury, an amalgam was formed, which, by distillation, afforded a white metal: when this metal was exposed to air, and gently heated, it burned, and produced *oxide of calcium*, or *lime*. Our knowledge of calcium is almost limited to this single experiment, and it has never been obtained in sufficient quantity to ascertain its general properties: its *equivalent*, as determined by evidence to which we shall presently recur, may be considered as = 20. 20·5, BERZELIUS. 20·5, TURNER. 20, GMELIN. 20, DUMAS. (*Comptes rendus*, xiv. 546.) 20, ERDMANN and MARCHAND, (*Ann. Ch. et Ph.*, Juin, 1843.)

OXIDE OF CALCIUM. LIME. QUICK LIME. CaO. Lime may be obtained in a state of considerable purity by exposing powdered white marble to a white-heat for an hour, in an open crucible, which expels the carbonic acid. To obtain absolutely pure lime, white marble may be dissolved in dilute hydrochloric acid, a little caustic ammonia added to the solution, and filtered; carbonate of ammonia is then added, and the precipitate washed, dried, and exposed for a sufficient time to a white-heat. This exposure to heat must always take place in an open vessel, for in a close vessel, out of the contact of air, the decomposition of carbonate of lime is very imperfect: indeed, powdered marble may be kept for many hours at a red-heat, without losing any carbonic acid, provided air and moisture be carefully excluded; but when a current of air or steam is passed over it, they constitute a medium into which carbonic acid has a tendency to diffuse. (See p. 138 and 300; also GRAHAM's *Elements*, p. 187.) To obtain lime perfectly free from all traces of carbonic acid, the carbonate should first be heated in an open vessel, the lime thus obtained converted into a *hydrate*, and this again heated: all residuary carbonic acid is thus effectually expelled.

Pure lime is white, or of a very pale grey tint; it is acrid and caustic, and has a powerful alkaline reaction on the usual tests; its specific gravity is 3·08 (DUMAS), 3·2 (RICHTER): it is very difficult of fusion, but remarkably promotes the fusion of some other oxides, and is therefore used in several metallurgic processes as a cheap and powerful flux. When quite pure it can only be fused in very minute particles by the oxygen blow-pipe, or by the Voltaic flame. When intensely heated, as, for instance, by the oxyhydrogen blow-pipe, it is remarkable for its luminosity; and at this very high temperature a minute quantity is volatilized (p. 127). It is an essential ingredient in mortar and other cements used

in building. Exposed to air it absorbs water and then carbonic acid, and losing its causticity becomes partially converted into carbonate of lime; so that when used for agricultural purposes it should, generally speaking, be speedily ploughed in, and not left in heaps upon the surface so as to acquire carbonic acid: in its caustic state it is most active in the destruction of vermin, and in effecting chemical changes upon the organic and inorganic constituents of the soil. Its powerful affinity for water renders it useful in various cases of dehydration, as in drying certain gases, and abstracting the water from alcohol and some other liquids: in the state of hydrate, or diffused through water (cream and milk of lime,) it is also used as an absorbent of carbonic acid: when perfectly dry it does not absorb that gas. Lime, being the protoxide of calcium, consists of

						Berzelius.	Davy.
Calcium	1	20	71·43	71·91	72·8
Oxygen	1	8	28·57	28·09	27·2
<hr/>							
Lime	1		28		100·00	100·00	100·0

HYDRATE OF LIME. SLAKED LIME. CaO,HO . When a small quantity of water is poured upon lime, a great rise of temperature ensues from the solidification and combination of a portion of the water, and a bulky white powder is obtained, which is a *hydrate*. The rise of temperature is so great when large heaps of good lime are suddenly slaked, as to inflame gunpowder and scorch wood; it certainly exceeds 500° , and when the operation is performed in a dark place light is also evolved. (PELLETIER.) When ice, or snow, and lime are mixed, there is a similar production of heat, so that the effect cannot be regarded as merely dependent upon the evolution of the latent heat of the water; it is also partly the result of chemical combination.

Hydrate of lime may be obtained in a crystalline form by placing lime-water under the receiver of an air-pump, containing another vessel of sulphuric acid. The water is thus slowly evaporated, and imperfect six-sided crystals are formed. (GAY LUSSAC, *Ann. Ch. et Ph.*, i. 334.) In composition these crystals resemble the pulverulent hydrate. Exposed to the air, they gradually crumble down into carbonate of lime. Hydrate of lime is a compound of

						Dalton.	Gay Lussac. <i>Crystallized.</i>
Lime.....	1	28	75·7	75	76·25
Water	1	9	24·3	25	23·75
<hr/>							
Hydrate of lime	1		37		100·0	100	100·00

LIME-WATER. At a temperature of 60° , 750 parts of water are required for the solution of one part of lime. Boiling water, however, as Dalton first observed (*New System of Chem. Phil.*), does not dissolve so large a quantity; one part of lime requires, according to Phillips, 1280 parts of water at 212° for its solution (*Ann. of Phil. N.S.*, i. 107); and water at 32° has its solvent power much augmented, one part of lime being soluble in 656 of water at that temperature. When lime-water is boiled, a portion of the lime is therefore precipitated; or aggregated, according to Phillips, into small crystalline grains. The cause of this crystallization he refers “to the effect which heat sometimes produces, of

increasing instead of diminishing the attraction of cohesion, where this attraction is associated with a tendency to crystallize. This crystalline attraction, increased by that of the lime for a definite portion of water, is then greater than the attraction of the hydrate of lime for the water of solution, and the consequence is that crystals are formed." Lime-water is limpid and colorless; its taste is nauseous and alkaline, and although the quantity of lime which it contains is relatively small, its alkaline reaction upon tests is very marked; it powerfully reddens turmeric, and changes the blue of violets and cabbage liquor to green. It is usually prepared by pouring warm water upon powdered lime, and allowing the mixture to cool in a close vessel; the clear part is then decanted from the remaining undissolved portion of lime; but Kühlmann observes, that as common lime contains small quantities of the salts of potassa and soda, the water first poured upon it may hold caustic potassa and soda and some of their salts in solution; to these he ascribes the stronger alkaline taste and reaction of such lime-waters; the purer lime-water is obtained by employing the hydrate of lime from which the first washings have been poured off. When lime-water is exposed to the air, a pellicle of carbonate of lime forms upon its surface, which, if broken, is succeeded by others, until the whole of the lime is thus separated in the form of an insoluble carbonate. Lime-water is used in medicine as an antacid.

PEROXIDE OF CALCIUM. BINOXIDE OF CALCIUM. CaO_2 . A hydrated peroxide of calcium is thrown down in the form of small brilliant scales, according to Thenard, when lime-water is dropped into oxygenated water. (*Ann. Ch. et Ph.*, viii. 313.)

CHLORIDE OF CALCIUM. MURIATE OF LIME. CaCl . This compound occurs in sea-water and in some saline springs and mineral waters, where it is generally accompanied by traces of bromine and sometimes of iodine. It is formed by heating lime in chlorine, in which case oxygen is evolved equal in volume to half that of the absorbed chlorine. It is also formed when carbonate of lime is decomposed by the action of hydrochloric acid ($\text{CaO}, \text{CO}_2 + \text{HCl} = \text{CaCl} + \text{HO} + \text{CO}_2$), the resulting solution is evaporated to dryness, and the residue exposed to a red heat in closed vessels. It has a strong attraction for water; it soon deliquesces when exposed to air, and becomes what used to be called *oil of lime*. Hence it is that fused chloride of calcium, broken into small pieces, is frequently employed to deprive gases of their aqueous vapor; but when thus used, its absorptive powers in regard to some gases must not be overlooked. It has also been remarked that by fusion it acquires a slight degree of alkalinity from partial decomposition; hence in accurate hygrometric analyses the strongly dried salt has been preferred to that which has undergone fusion. It is also in consequence of its affinity for water that it is used occasionally as a means of depriving alcohol, ether, and other liquids, of water, for which purpose they are generally distilled off dry chloride of calcium. Its taste is bitter and acrid. One part of water at 60° , dissolves four parts of this chloride; its solubility, however, is greatly influenced by temperature, for at 32° one part of water will not dissolve more than two of the salt, and at 212° it takes up nearly any quantity. It is copiously soluble in alcohol, and much heat is evolved during the

solution. Ten parts of anhydrous alcohol dissolve seven of chloride of calcium at the boiling-point, and the solution in cold weather affords crystals in rectangular scales, which are an *alcoate* containing about 60 *per cent.* of alcohol instead of water of crystallization. (GRAHAM.) When fused it acquires a phosphorescent property, as was first observed by Homberg, and hence it was termed *Homberg's phosphorus*. It is produced in the manufacture of carbonate of ammonia, from the decomposition of hydrochlorate of ammonia by lime, and hence it was formerly called *fixed sal-ammoniac*. (See pp. 439 and 468.) Chloride of calcium consists of

						Ure.	Döbereiner.		
Calcium.....	1	...	20	...	35·7	...	36·7	...	38·46
Chlorine	1	...	36	...	64·3	...	63·3	...	61·54
<hr/>									
Chloride of calcium	1		56		100·0		100·0		100·00

Pelletier says that when carbonic acid is passed through a solution of chloride of calcium, the whole becomes a hard solid mass. If sulphuric acid be poured into a strong solution of chloride of calcium, the whole congeals into a solid mass of sulphate of lime, and hydrochloric acid escapes. A solution of chloride of calcium is used in medicine as an alterative, especially in scrofulous glandular affections.

HYDRATED CHLORIDE OF CALCIUM is obtained by evaporating the aqueous solution to the consistence of a thick syrup ; on cooling, it concretes into a crystalline mass, which may be reduced to powder, which is $\text{CaCl}_2\cdot 2\text{HO}$; in this state it is used in frigorific mixtures, to mix with snow. (p. 69.) By exposing a strong aqueous solution of chloride of calcium to a cold of 32° , it yields striated four-sided prisms $= \text{CaCl}_2\cdot 6\text{HO}$, or consisting of

							Berzelius.
Chloride of calcium	1	...	56	...	50·9	...	50·4
Water	6	...	54	...	49·1	...	49·6
<hr/>							
Crystallized hydrated chloride of calcium	1		110		100·0		100·0

OXYCHLORIDE OF CALCIUM. When hydrate of lime is boiled in a solution of chloride of calcium, it is dissolved, and if the solution be filtered while hot, it deposits flat prismatic crystals which contain 49 *per cent.* of water, and which are decomposed both by water and alcohol. These crystals are composed of 3 equivalents of lime, 1 of chloride of calcium, and 15 of water.

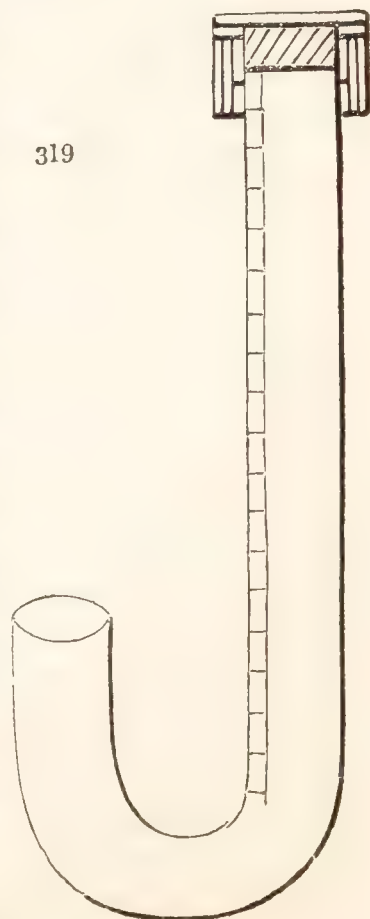
AMMONIOCHLORIDE OF CALCIUM. Faraday has shown (*Quart. Journ.*, v. 74) that chloride of calcium absorbs large quantities of ammoniacal gas, during which it swells, cracks, splits in all directions, and at last crumbles down into a white powder. Exposed to the atmosphere, it deliquesces less rapidly than the original chloride. Thrown into water it dissolves, forming a strong alkaline solution. Heated, it gives off ammonia, and the chloride remains unchanged. Immersed into chlorine, the ammonia burns off spontaneously with a pale-yellow flame. Faraday found that 19 grains of this compound gave off 19·4 cubic inches of ammonia, which would indicate it as a compound of 1 equivalent of chloride of calcium $= 56$, and 1 of ammonia $= 17$. But according to H. Rose

(*Poggend.*, xx., 154), when the chloride is saturated by ammonia, it is $\text{CaCl}_2 \cdot 4\text{NH}_3$: that is, it contains 55 *per cent.* of ammonia.

CHLORIDE OF LIME. OXYMURIATE OF LIME. HYPOCHLORITE OF LIME. This compound is abundantly employed as a bleaching material; it was first manufactured by Mr. Tennant, of Glasgow, who obtained a patent for it in 1799; it was made by passing chlorine into chambers containing hydrate of lime in fine powder, by which the gas is copiously absorbed, care being taken to suppress the extrication of heat. An account of the apparatus and machinery employed by the wholesale makers of this article, together with remarks upon its composition and analysis, will be found in URE's *Dictionary of Arts and Manufactures*. It is a dry white powder, smelling feebly of chlorine, and having an acrid taste: it is partially soluble in water, and the solution is used under the name of *bleaching-liquor*. Exposed to air it slowly evolves chlorine (or hypochlorous acid,) and absorbs carbonic acid; ultimately some chloride of calcium is formed, and it deliquesces. When heated, it gives off oxygen, and chloride of calcium results, an experiment which shows the superior attraction of calcium for chlorine as compared with oxygen, the latter being expelled from the lime.

The solution obtained by digesting bleaching-powder in distilled water has a strong alkaline reaction upon most of the usual tests, and its bleaching power is only slowly developed unless some acid be added, when it is powerful and immediate: thus it is that the calico-printers produce white figures upon colored ground, by printing the pattern intended to be brought out upon the colored calico, in citric or tartaric acid thickened with starch or gum; the goods are then rapidly wound through a properly adjusted solution of chloride of lime, and the bleaching power only shows itself where the acid pattern had been previously applied; in the same way a solution of the chloride may be colored blue by litmus, or green by red cabbage, or brown by turmeric, and on the addition of a few drops of acid the color immediately disappears. By exposure to air the absorption of carbonic acid effects the same change, and the evolution of that acid in respiration is well shown by tinging a weak solution of chloride of lime blue by litmus, and then breathing through it by means of a tube, when the blue color gradually disappears. (TAYLOR.)

Dr. Ure has contrived an instrument for the speedy analysis of bleaching-powder for the purposes of the manufacturer, by which the quantity of chlorine in any given sample may be determined. (*Quart. Journ.*, xiii. 21.) "It consists of a glass tube, of about five cubic inches capacity, shaped as in the adjoining figure, and graduated into cubic inches and tenths. It is to be closed at top with a brass screw cap, and, at its recurved end below, with a good cork. Pour mercury into the upper orifice, till the tube be nearly full, leaving merely space to insert ten grains of the bleaching-



powder, made into a pellet-form with a drop of water. Screw in the cap-plug rendered air-tight by leather. Remove now the cork from the lower end, (also full of mercury,) and replace a little of the liquid metal by dilute hydrochloric acid (specific gravity 1.1.) By dexterous inclination of the instrument, the acid is made to flow up through the mercury. Instantly on its coming into contact with the pellet, the chlorine is disengaged, the mercury flows out into a basin ready to receive it, while the resulting film of muriate of lime protects the surface of the metal almost completely from the gas. With an apparatus of this kind, which indeed is the same as that which I have long used for analyzing limestones and marbles, I get good accordances with the results derived from the loss of weight suffered by a like quantity of the chloride, when it is dissolved in dilute hydrochloric acid. Since a cubic inch of chlorine may be estimated in round numbers at $\frac{3}{4}$ of a grain, we may expect 10 grains of bleaching-powder to yield from 3 to 4 cubic inches of that gas, or by weight from 20 to 30 *per cent.*, a wide range of power, which it is well worth the bleacher's or paper-maker's while to ascertain. If carbonic acid be suspected, we need only agitate the mercury through the gas, adding some of the metal from time to time as the absorption proceeds. The carbonic acid will remain undensified at the top, and may be estimated in the usual way."

Another mode of determining the commercial value of chloride of lime, consists in ascertaining its bleaching power by its effect upon a standard solution of indigo; directions for this purpose have been drawn up by Gay Lussac. (*Ann. of Phil.*, xxiv. 218.) Morin (*Ann. Ch. et Ph.*, xxxvii. 142) tests it by solution of protochloride of manganese, determining its proportion of chlorine by the quantity of peroxide of manganese which it throws down; but the free lime present interferes with the practical application of this test. More lately Gay Lussac has proposed the conversion of arsenious into arsenic acid by the influence of chlorine as a test of the value of bleaching-powder. The similar conversion of protosulphate into persulphate of iron has also been resorted to.

The following are Kane's directions for the use of the arsenical and the iron tests:—

"100 grains of arsenious acid are to be dissolved in 2000 grains of strong hydrochloric acid, and this liquor diluted with distilled water till it occupies the volume of 7000 grains of water: this is the standard test liquor; to employ it, 100 grains of the bleaching-powder to be tested are to be diffused through 1000 grains of water, and the test liquor to be gently poured from a graduated glass on it, in a deep jar, continually stirring the mixture; a drop of weak solution of sulphate of indigo is to be occasionally applied by means of a glass rod to the surface of the liquor; as long as any chlorine remains unaltered, the blue color of the drop is instantly destroyed, and the addition of the arsenic liquor is to be continued until the blue drop remains unaltered. Then the quantity of chlorine present in the 100 grains of bleaching-powder is represented by $\frac{1}{100}$ th of the quantity of the test liquor employed; thus, if there were 2565 grains of the test liquor necessary to destroy the bleaching power of the 100 grains of the chloride of lime, the quantity of chlorine would be 25.65. This is not absolutely correct, for in theory the true quantity of chlorine indicated would be 26.08; but as a few drops of the solution are

always employed more than what should by theory be necessary, the practical proportion of $\frac{1}{100}$ th comes very near the truth. Even one-half part *per cent.*, which is the limit of error, is quite unimportant in practice." (*Elements of Chemistry*, 712.)

"390 grains of clean and dry crystals of green sulphate of iron are to be dissolved in as much water as will bring the solution to the volume of 5000 grains of water. On the other hand, 100 grains of the chloride of lime is to be diffused through 1000 grains of water, and the iron solution is to be added thereto, until the presence of a trace of the protosulphate of iron in excess is indicated by the mixed liquor striking a full blue color when a drop of it is placed on a slip of paper imbibed with *red prussiate of potash*. The quantity of chlorine present in the 100 grains of the bleaching-powder is $\frac{1}{100}$ th of the quantity of the standard iron solution employed: thus if 2783 grains measure of the volume of the solution be found necessary, the sample contains 27.83 of chlorine *per cent.*: for the 2783 of liquor contains 217 grains of sulphate of iron, which is peroxidized by the action of 27.6 grains of chlorine; here also the limit of error need not exceed one-half *per cent.*"

Of these methods I have practically found the former most effective; in reference to the latter, see also Graham (*Elem. Chem.*, 502.)

The composition of bleaching-powder has been variously stated. Dalton (*Ann. of Phil.*, i. 15, and ii. 6) considers it as a *hydrated subchloride of lime*, containing 2 proportionals of lime and 1 of chlorine; and the same opinion is adopted by Thomson (*Ann. of Phil.*, xv. 401,) and by Welter. (*Ann. Ch. et Ph.*, vii. 383.) Dr. Ure shows, in the paper already quoted, that the quantity of chlorine absorbed is variable: he analyzed a specimen of good commercial bleaching-powder, and found it composed of 46 lime, 23 chlorine, and 31 water: a specimen prepared by himself with pure hydrate of lime contained 45.40 lime, 40.32 chlorine, and 14.28 water; and he found the condensation of chlorine to vary with the pressure, the degree of exposure, and the quantity of water present. From these statements it would seem not improbable that bleaching powder contains 1 proportional of chlorine and 1 of lime, mixed with a varying quantity of hydrate of lime; and that when water acts upon the compound the solution contains a chloride of lime. Berzelius regards bleaching-powder as a compound of chloride of calcium and *chlorite* of lime, and this opinion is said to be sanctioned by Balard's researches already quoted (p. 280,) but in opposition to this view, it has been observed, that if chlorite or hypochlorite of lime were formed by the action of chlorine upon pulverulent hydrate of lime, chloride of calcium must at the same time be produced, and we have no evidence of the existence of more than a trace of chloride of calcium in well-made bleaching-powder. More lately this subject has been studied by Millon (*Jour. de Pharm.*, September, 1839,) but without any important practical results; he, however, finds that many of the precipitates formed in metallic solutions by the addition of a solution of chloride of lime, consist of 1 equivalent of the metallic oxide combined with 1 of chlorine; as if, therefore, setting out with the binoxide of a metal, 1 equivalent of oxygen had been replaced by 1 of chlorine.

Gay Lussac, in a paper "on the combinations of chlorine with bases," (*Ann. Ch. et Ph.*, 3d. Ser., v. 273, already quoted in reference to the

composition of *hypochlorous acid*,) has rendered it extremely probable that bleaching-powder contains a true hypochlorite of lime; he observes, that if it were a chloride of lime, the addition of a small quantity of sulphuric acid ought immediately to evolve chlorine, whereas he shows that hypochlorous acid, and not chlorine, is in that case set free; that the bleaching power of hypochlorous acid is very great; and that free chlorine is only evolved when excess of sulphuric acid is added, by which the hypochlorous acid is decomposed. If bleaching-powder, instead of being a compound of hydrated lime and chlorine, or a chloride of lime, be a compound of chloride of calcium and hypochlorite of lime, the first effect of a stronger acid upon it, (such as sulphuric,) would be the expulsion of hypochlorous acid, and the formation of sulphate of lime, which would remain mixed with the undecomposed chloride of calcium. Thus the original powder being $\text{CaCl} + \text{CaClO}$, the action of 1 equivalent of sulphuric acid would produce $\text{CaCl} + \text{CaO}, \text{SO}_3 + \text{ClO}$; but with 2 equivalents of sulphuric acid the whole of the chlorine would be expelled, and sulphate of lime formed at the expense of the chloride of calcium, as well as of the hypochlorite of lime; for $\text{CaCl} + \text{CaO}, \text{ClO} + 2\text{SO}_3$ would give $2\text{CaO}, \text{SO}_3$ and 2Cl .

In its perfect state, therefore, bleaching-powder may be a hydrated chloride of lime $= \text{CaO}, \text{Cl}, \text{HO}$, or a compound of hydrated hypochlorite of lime with chloride of calcium $= \text{CaCl}, \text{CaOClO}, 2\text{HO}$.

Lime.....	1	28	38·35	} or {	Chloride of calcium....	1	56	38·35
Chlorine	1	36	49·31		Hypochlorite of lime	1	72	49·31
Water	1	9	12·34		Water	2	18	12·34
	1		73		100·00			1		146		100·00

But the best samples of commercial chloride of lime contain on the average not more than 30 *per cent.* of chlorine, and when chlorine is passed over hydrate of lime in an experiment upon the small scale, it cannot be made to absorb more than about 40 *per cent.*; but if the hydrate of lime be diffused through water, it will then absorb more than its own weight of chlorine, and we form a solution containing 1 equivalent of lime (or of hydrate of lime,) and 1 of chlorine, which is the true atomic compound, and is dissolved out of bleaching-powder by the action of water. The usual bleaching-powder, therefore, may be regarded as containing

Chlorine.....	1	36	32·72
Hydrate of lime	2	74	67·28
Bleaching-powder	1		110		100·00

When put into water, 1 atom of hydrate of lime remains undissolved, and the above-mentioned solution, containing 1 atom of lime and 1 of chlorine, is formed. It may be observed, in regard to the theory of the composition of bleaching-powder, that the extreme slowness with which it absorbs moisture, so as to deliquesce, and the facility with which it is decomposed by carbonic acid, are in favor of considering it as a chloride of lime.

CHLORATE OF LIME, CaO, ClO_5 , is a very soluble deliquescent salt of a sharp bitterish taste, difficultly crystallizable in oblique rhombic prisms,

soluble in alcohol, and imparting a red color to its flame. During its solution in water, it produces cold. It is most easily formed by dissolving carbonate of lime in chloric acid. Exposed to heat, oxygen is evolved, and a chloride remains. The crystals probably contain 2 atoms of water.

PERCHLORATE OF LIME, CaO, ClO_7 , is extremely deliquescent: it is soluble in alcohol, to the flame of which it gives a red tinge. (SERULLAS, *Ann. Ch. et Ph.*, XLvi. 304.)

IODIDE OF CALCIUM, CaI , is obtained by dissolving carbonate of lime in hydriodic acid, evaporating to dryness, and heating the residue in a close vessel till it fuses; it may also be obtained by digesting hydrate of lime with protiodide of iron: it is a deliquescent grey substance, which, heated in the air, absorbs oxygen and evolves iodine.

Dissolved in water and slowly evaporated, it furnishes deliquescent crystals, usually called *hydriodate of lime*; they are composed of the iodide and water. The iodide consists of

Calcium	1	20	13.8
Iodine	1	126	86.2
<hr/>					
Iodide of calcium	1		146		100.0

When iodine vapor is passed over lime heated to redness in a porcelain tube, a compound is formed without any evolution of oxygen, the aqueous solution of which is alkaline: at a very high temperature it gives out iodine. (GAY LUSSAC. GROUVELLE.)

IODATE OF LIME. CaO, IO_5 . This salt is formed by dissolving carbonate of lime in iodic acid; it also gradually separates out of a mixed solution of iodate of potassa and chloride of calcium: it forms prismatic crystals, containing 18 *per cent.* of water, and requiring 253 parts of water at 60° , and 75 parts at 212° , for their solution. (RAMMELSBERG, *Poggend.*, XLiv.)

BROMIDE OF CALCIUM, CaBr , was obtained by Henry by digesting hydrate of lime in a solution of protobromide of iron. It is also formed by heating lime in bromine vapor, or by dissolving carbonate of lime in hydrobromic acid, and evaporating to dryness: it is white, deliquescent, soluble in alcohol, and its aqueous solution yields silky hydrated crystals.

BROMATE OF LIME, CaO, BrO_5 , has been examined by Rammelsberg; it is soluble in a little more than its weight of water, and forms crystals $= \text{CaO}, \text{BrO}_5, \text{HO}$. (*Poggend.*, Lii. 88.)

FLUORIDE OF CALCIUM. FLUOR-SPAR. CaF . This compound may be produced artificially by saturating dilute hydrofluoric acid with newly-precipitated and moist carbonate of lime, and may thus easily be collected, and dried in the form of white powder. If obtained by precipitating a neutral salt of lime with a soluble fluoride, it forms a gelatinous mass, the precipitation of which is accelerated by the addition of caustic ammonia.

Native fluoride of calcium, or fluor-spar, is a mineral found in many

parts of the world, but in great beauty and abundance in England, and especially in Derbyshire, where it is commonly called *blue John*. It is usually found in cubic crystals, which may easily be cleaved into octohedra, and tetrahedra (p. 21). Its colors are extremely various. Its specific gravity = 3. It phosphoresces when exposed to a heat a little below redness (p. 120), and at a red heat it fuses: it is sometimes used as a flux for promoting the fusion of other minerals, hence its German name *Flus-spath*, and the English *Fluor*. It generally occurs in veins; in the Odin mine at Castleton, in Derbyshire, it is found in detached masses, from an inch to more than a foot in thickness; their structure is divergent, and the colors, which are various, disposed in concentric bands. It is the only variety which admits of being turned in the lathe into vases and other ornamental articles. *Compact fluor* is a scarce variety; the finest specimens come from the Hartz. A third variety is *chlorophane*, so called from the beautiful pale-green light which it exhibits when heated. The nature of the coloring-matter of blue and green fluor-spar is not understood: it is liable to fade, and the blue varieties become red and brown by heat.

Fluoride of calcium exists, according to Berzelius, in bones, urine, and the enamel of the teeth, in the human subject; it has been found in some fossil bones to the extent of 10 *per cent*. He also found it in minute quantities in some of the Carlsbad waters, but it appears probable that at least in some of these cases the phosphate of lime has been mistaken for it.

Pure fluoride of calcium is not decomposed by cold sulphuric acid, but forms with it a transparent viscid mixture. At a temperature of about 100° its decomposition begins, sulphate of lime forms, hydrofluoric acid is evolved, and the mixture grows opaque. If the fluor-spar contain silica, then sulphuric acid immediately acts upon it, evolving silicofluoric acid. Concentrated hydrochloric and nitric acids dissolve fluoride of calcium without decomposition, and become milky when diluted; but it is doubtful whether such solutions are formed when the fluoride is perfectly pure. It is scarcely soluble in hydrofluoric acid. Fused with carbonate of potassa, carbonate of lime and fluoride of potassium are produced. It is now generally admitted to be a binary compound of calcium and fluorine, consisting of

							Davy.
Calcium	1	20	51.54	53.313
Fluorine	1	19	48.46	46.637
<hr/>							
Fluoride of calcium	1		39		100.00		100.000

NITRATE OF LIME. CaO, NO_5 . This is a deliquescent salt, soluble in one-fourth its weight of water at 60° . It is found in old plaster and mortar, from the washing of which, nitre is procured by the addition of carbonate of potassa. It sometimes occurs in spring water; I have detected it in several samples from the vicinity of London. Berzelius mentions it as accompanying nitrate of magnesia, in the well-waters of Stockholm.

The production of this salt in artificial nitre-beds has already been adverted to (p. 573). It may be crystallized, by very slow evaporation, in six-sided prisms, containing, according to Hess and Millon, about 30 *per cent*. of water, $= \text{CaO}, \text{NO}_5, 4\text{HO}$; when obtained from a solution

evaporated very low, and set aside in the cold, it appears in the form of groups of acicular crystals. It is soluble in an equal weight of boiling alcohol. When exposed to a moderate heat, it undergoes watery fusion; the water then evaporates and the salt fuses; on cooling it concretes into a semi-transparent phosphorescent substance, called from the discoverer of this property *Balduin's phosphorus*. (BIRCH'S *History of the R.S.*, iii. 328. See also p. 119.) At a red heat it is decomposed; its acid is dissipated, and pure lime remains. Anhydrous nitrate of lime consists of

						Wenzel.	Longchamp.
Lime	1	...	28	...	34.1	...	33.8
Nitric acid	1	...	54	...	65.9	...	66.2
<hr/>							
Nitrate of lime	1		82		100.0		100.0

SULPHURET OF CALCIUM, CaS , is formed by passing sulphuretted hydrogen over red-hot lime, when water is evolved. $\text{CaO} + \text{HS} = \text{CaS} + \text{HO}$. It is also formed by the action of charcoal or of hydrogen upon *sulphate of lime* at a red heat. It is of a reddish-white tint, slowly acted upon by water, forming a colorless solution of an hepatic and alkaline taste. When freshly prepared it is phosphorescent in a dark place, as was first observed by Canton (p. 119). It contains

Calcium	1	...	20	...	55.55
Sulphur	1	...	16	...	44.45
<hr/>					
Protosulphuret of calcium	1		36		100.00

BISULPHURET OF CALCIUM. CaS_2 . When sulphur and hydrate of lime, about equal weights, are boiled together in water, and the solution cooled, yellow prismatic crystals form, which, after having been dried in vacuo, are permanent: their taste is alkaline and sulphurous: they contain 1 atom of calcium, 2 of sulphur, and 3 of water: when gently heated in vacuo they become anhydrous, and the bisulphuret remains in the form of a white powder. The crystals require 400 parts of water at 60° for solution. (BERZELIUS.) The yellow solution, from which the crystals are deposited, retains hyposulphite of lime in solution. $6\text{S} + 3\text{CaO} = \text{CaO}, \text{S}_2\text{O}_2 + 2\text{CaS}_2$. By exposure to air it becomes colorless, in consequence of the further formation of hyposulphite. (See *Hyposulphite of Lime*, and *Hyposulphurous Acid*, p. 401.)

PENTASULPHURET OF CALCIUM. CaS_5 . When excess of sulphur is continuously boiled in water with quick-lime, a compound of 5 atoms of sulphur with 1 of calcium, is formed, which is not crystallizable: it is soluble in alcohol; and when its aqueous solution is evaporated in vacuo, it leaves a yellow mass containing about 80 *per cent.* of sulphur. By heat it loses sulphur, and becomes protosulphuret.

HYPOSULPHITE OF LIME. $\text{CaO}, \text{S}_2\text{O}_2$. When sulphurous acid is ground in a mortar with crystals of hydrated bisulphuret of lime, it loses its odor, and when filtered it is found to be a solution of *hyposulphite of lime*. By passing sulphurous acid through the yellow liquor obtained by boiling lime and sulphur together in water, the same product is obtained; and if the solution be filtered and evaporated, at a temperature not exceeding 140° , it furnishes hexagonal crystals: the temperature of ebullition de-

composes it into sulphite of lime and sulphur. The crystals are little altered by air, very soluble in water, and insoluble in alcohol. They consist of

				Herschel.
Lime	1	28 21·3
Hyposulphurous acid	1	48 36·8
Water	6	54 41·4
<hr/>				
Crystals of hyposulphite of lime.....	1		130	100·0

This salt is much employed as a means of removing the salts of silver from photogenic drawings, so as to render them permanent when exposed to light (see SILVER). Mr. Alfred Taylor, in his paper *On the Art of Photogenic Drawing*, directs its preparation for this purpose as follows: One ounce of sublimed sulphur is to be mixed with one ounce and a half of lime, previously slaked by the addition of hot water, and the mixture put into a clean earthen vessel. Three quarts of water are added, and the whole is to be boiled for two hours. The clear liquid may then be filtered off into several wide basins or dishes, and allowed to remain freely exposed to air. (The residue on the filter may, if required, be boiled with more slaked lime and water, until it ceases to yield a yellow-colored liquid.) When first made, the liquor is of a rich orange color, but a scaly semi-crystalline crust soon forms on its surface; this must be broken down as often as it is produced, and the liquid be exposed to air until it has become quite colorless. The time required for this, varies according to the depth of the color, and the quantity of persulphuret of calcium present in it. If weak, the change is complete in three or four days; if strong, the whole of the color will not be lost until after the lapse of three or four weeks. The change is always accelerated by diluting the liquid; but this must not be carried too far. When colorless, the liquid, which is now a solution of hyposulphite of lime, may be filtered off, and is fit for use. The scaly residue left on the filter, digested in cold water, will yield more of the hyposulphite.

The refuse lime of the gas-works is an abundant source of the hyposulphite: after removal from the purifier it should be exposed to air for two or three days, till it no longer smells of sulphuretted hydrogen: the hyposulphite may then be dissolved out by an equal weight of cold water, and crystallized after evaporation at 120° : or by carbonate of soda, it may be converted into the more stable *hyposulphite of soda*. (GRAHAM, *Mem. Ch. Soc.*, ii. 359.)

SULPHITE OF LIME, CaO,SO_2 , is formed by passing sulphurous acid into a mixture of lime and warm water, or by mixing the solutions of chloride of calcium and sulphite of potassa. It is a white powder of a slightly sulphurous taste; it requires about 800 parts of water at 60° for its solution: it is rendered soluble by excess of sulphurous acid, and then separates in hexangular prismatic crystals, of difficult solubility, efflorescent, and passing into sulphate of lime by exposure to air. When heated this salt is converted into sulphuret of calcium and sulphate of lime. It consists of

Lime	1	28 46·7
Sulphurous acid	1	32 53·3
<hr/>				
Sulphite of lime	1		60	100·0

HYPOSULPHATE OF LIME. $\text{CaO}, \text{S}_2\text{O}_5$. This salt is formed by decomposing hyposulphate of manganese by milk of lime, filtering, and evaporating the solution; it forms groups of transparent tabular crystals, permanent in the air, soluble in 0·8 of water at 212° , and in 2·46 of water at 60° , and insoluble in alcohol. (HEEREN, *Poggend.*, vii. 178.) The crystals consist of

Lime	1	28	20·6
Hyposulphuric acid.....	1	72	52·9
Water	4	36	26·5
<hr/>					
Crystals of hyposulphate of lime	1		136		100·0

SULPHATE OF LIME. CaO, SO_3 , occurs native in *selenite*, *gypsum*, *plaster-stone*, &c. It is easily formed artificially, by dropping sulphuric acid upon lime, in which case there is great evolution of heat; or by decomposing a solution of chloride of calcium, or any of the soluble salts of lime, by sulphuric acid or by a soluble sulphate. When thrown down from its solutions, or in any way slowly deposited, it often forms minute silky crystals soluble in 350 parts of water. When these, or the *native crystallized sulphate*, are exposed to a heat of from 4 to 500° , they lose water, and fall into a white powder (*plaster of Paris*), which, made into a paste with water, soon solidifies, and when in large quantity, with very sensible increase of temperature: hence its use in taking casts for busts, figures, and ornaments: it is also the basis of stucco and scagliola or artificial marble, which is made by mixing plaster of Paris, colored in various ways, with size and water; when it has indurated, its surface is polished. (On the influence of various salts upon its induration, see EMMET, *Ed. Phil. Journ.*, xv. 69.) Exposed to a red-heat, but short of its fusing-point, it loses this property of recombining with water. The sp. gr. of anhydrous sulphate of lime (artificial) is 2·927: it requires about 500 parts of water at 60° , and 450 parts at 212° , for its solution: or, according to Berzelius, it is equally soluble in cold and hot water, 1 part of the salt being soluble in 462 of water, or in 332, according to Lassaigne. This aqueous solution even when made with the native crystallized sulphate, slightly reddens litmus. (LAUGIER, *Journ. de Ch. Med.*) According to Mr. Paul (*Phil. Mag.*, xv. 63), if this solution be saturated by pressure with hydrogen, the sulphate in about six months is converted into a sulphuret. Like the other sulphuric salts it is slowly decomposed when its solution is subjected to the action of decaying vegetable matter, in which case the odor of sulphuretted hydrogen becomes apparent. As sulphate of lime is more soluble in water than pure lime, sulphuric acid affords no precipitate when added to *lime-water*. Nearly all spring and river water contains traces of this salt, and in those waters which are called *hard* it is often abundant: it gives to them a slightly nauseous taste, and renders them unfit for washing and for culinary use. At a very high temperature sulphate of lime is fusible, but suffers no decomposition; heated with charcoal it is converted into a sulphuret of calcium. It dissolves without decomposition in dilute nitric and hydrochloric acids, and separates from these solutions when concentrated, in long silky or transparent crystals. It is decomposed by the alkaline carbonates. Sulphate of lime is sometimes employed as a manure, and, when sprinkled over the land in small quantity, is said to improve certain

soils, especially for the growth of clover: it may also be useful with other crops as a source of sulphur. Anhydrous sulphate of lime consists of

						Wenzel.	Bergman.	Berzelius.			
Lime	1	...	28	...	41·2	...	40·2	...	41	...	42
Sulphuric acid ...	1	...	40	...	58·8	...	59·8	...	59	...	58
<hr/>											
Sulphate of lime	1		68		100·0		100·0		100		100

And the native crystallized sulphate of lime consists of,

						Klaproth.	Bergman.	Bucholz.		
Anhydrous sulphate of lime	1	68	79	78	79
Water	2	18	21	22	21
<hr/>										
Crystallized sulphate of lime	1		86		100		100		100

A *dihydrated sulphate of lime* = 2[CaO,SO₃]HO, has been described by Johnston forming a deposit in a high pressure steam-boiler, in the form of a grey granular mass, sp. gr. 2·757, made up of minute transparent prisms colored by carbonaceous matter. (*Phil. Mag.*, xiii. 325.)

Native Sulphate of Lime occurs in various forms. The *crystallized* or *hydrous* variety, CaO,SO₃,2HO, is usually called *selenite*, (from *σεληνη*, the moon, in reference to its soft lustre); the fibrous and earthy, *gypsum*, (from *γη*, earth, and *εψειν*, to concoct: formed or concocted in the earth); and the granular or massive, *alabaster*, (an ancient term applied to vases or boxes, for containing perfumes: perhaps from *a*, privative, and *λαβον*, a handle, as opposed to vessels *with* handles.) The primitive form of selenite is a rhomboidal prism of 113° 8' and 66° 2'. The crystals are commonly transparent, of a specific gravity of 2·32, and of various colors; softer than native carbonate of lime, and yield very easily to the nail. They are often disseminated in argillaceous strata. It occurs in Cumberland at Alston, and in Oxfordshire at Shotover Hill, where it is accompanied by shells and pyrites, and appears to have resulted from their mutual decomposition. A beautiful fibrous variety, called *satin gypsum*, is found in Derbyshire, applicable to ornamental purposes, such as beads, brooches, &c. *Massive and granular gypsum* is found in this country in the red marl or new red sandstone accompanying the salt-deposits in Cheshire. It abounds in the tertiary strata of Montmartre, near Paris, and contains organic remains; sometimes it forms entire hills. In the Tyrolese, Swiss, and Italian Alps, it is found upon the primitive rocks, often of the purest white, especially at Montier, near Mont Blanc, and near the summit of Mont Cenis. It is turned by the lathe, and sculptured into a variety of beautiful forms, more especially by the Florentine artists. Columns for interior architecture are sometimes formed of it.

There is a variety of sulphate of lime which has been called *anhydrous gypsum*, or *anhydrite*, in reference to its containing no water. It is harder and denser than selenite, its specific gravity being 2·96: it sometimes contains common salt, and is then called *muriacite*. It is rarely crystallized, generally massive and lamellar, and susceptible of division into rectangular prisms. It has been found in Derbyshire and Nottinghamshire of a pale-blue tint; sometimes it is pink or reddish, and often white. It has also been found at Vulpino in Italy, and hence called *Vulpinite*. The statuaries of Bergamo and Milan employ it, and

artists know it by the name of *Marbre di Bergamo*. A compound of sulphate of lime and sulphate of soda is found in the salt mines of New Castile, which mineralogists have described under the name of *Glauberite*, and which probably might be formed artificially by fusing the two salts.

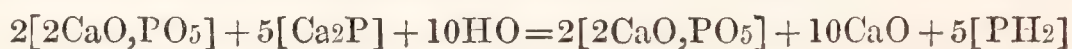
PHOSPHURET OF CALCIUM. CaP . By passing the vapor of phosphorus over lime heated to dull redness a brown compound is produced, usually called *phosphuret of lime*: it rapidly decomposes water with the evolution of phosphuretted hydrogen gas, and consists of phosphuret of calcium and phosphate of lime; the oxygen of the lime at this temperature converts a portion of the phosphorus into phosphoric acid, and the evolved calcium combines with another portion of phosphorus to form phosphuret of calcium. *Hydrophosphuret* and *hypophosphite of lime* are formed by its action upon water, phosphuretted hydrogen gas escapes, and a phosphate of lime precipitates. When dilute hydrochloric acid is poured upon this phosphuret, *phosphuretted hydrogen* is also liberated (p. 433).

The usual process for obtaining phosphuret of calcium is the following: Select a green-glass or porcelain tube, closed at one end, and about eighteen inches long, and one inch diameter, and carefully cover it with a clay lute containing a very little borax. Put an ounce of phosphorus broken into small pieces into the lower end, and fill it up with pieces of clean quick-lime, about the size of large peas: place it in an inclined position in a furnace, so that the end containing the phosphorus may protrude, while the upper part of the tube is heating; then slowly draw the cool part into the fire, by which the phosphorus will be volatilized, and, passing into the hot lime, convert a portion of it into phosphuret. Care should be taken that no considerable portion of phosphorus escapes and burns away at the open end of the tube, which, after the process, should be corked and suffered to cool. Its contents may then be shaken upon a sheet of paper, and the brown pieces picked out, and carefully preserved in a well-stopped phial; the white pieces, or those which are only pale-brown, must be rejected. The success of this operation depends upon the skilful management of the temperature, and the difficulty of heating the whole of the lime up to a proper point, which should be short of a red-heat; for if the temperature be insufficient, no combination ensues; and if too high, the compound is again decomposed, phosphorus evolved, and lime remains. According to Berzelius, phosphuret of lime is best obtained by heating pieces of lime in a long-necked matrass over the flame of a spirit lamp and dropping phosphorus upon them. When the compound is perfect it is reddish-brown or chocolate-colored; when breathed on or moistened it exhales a very strong and diffusive alliaceous odor, which it is difficult to get rid of; it heats and even burns if touched with damp hands, and when dropped into water the action is immediate and often violent, and the evolution of phosphuretted hydrogen continues for some time.

In a memoir on the combinations of phosphorus with hydrogen, by Paul Thenard (*Ann. Ch. et Ph.*, Mai, 1845), an apparatus for the preparation of phosphuret of lime upon the large scale is described, and the properties and composition of the product carefully examined. When properly prepared it is of a cinnabar-red color, and very hard, seeming to

have undergone semifusion: it is unchanged at common temperatures by dry air, hydrogen, and carbonic acid: at a high temperature oxygen, chlorine, and hydrochloric acid, decompose it: in humid air it soon falls into a brown powder, and forms phosphuretted hydrogen: this powder thrown into boiling water disengages large quantities of phosphuretted hydrogen (not spontaneously inflammable) and hydrogen; when highly concentrated nitric acid is dropped upon it, it inflames and explodes: it is kindled by the flame of a taper, and leaves a white residue. The original phosphuret reduced to powder exhibits the same properties: it is converted by sulphuric acid into phosphate, and sulphurous acid is evolved.

From his experiments on the composition of the so-called phosphuret of lime, he concludes that it contains 2 equivalents of neutral phosphate of lime, and 5 of phosphuret of calcium = Ca_2P ; so that its formula will be $2[2\text{CaO}, \text{PO}_5] + 5[\text{Ca}_2\text{P}]$; when acted upon by water the 10 equivalents of calcium in the phosphuret combine with 10 of oxygen to form 10 of lime, and are replaced by 10 equivalents of hydrogen to form a new phosphuret of hydrogen = P_5H_{10} , or $5[\text{PH}_2]$.



This new phosphuret of hydrogen is a liquid which spontaneously resolves itself into a *solid phosphuret*, and *phosphuretted hydrogen gas*, the solid phosphuret being a compound of 2 atoms of phosphorus and 1 of hydrogen, the formula of this spontaneous decomposition being $5[\text{PH}_2] = \text{P}_2\text{H} + 3[\text{PH}_3]$. Thenard ascribes the spontaneous inflammability of phosphuretted hydrogen to the presence in it of a very minute quantity of the vapor of the above liquid phosphuret.

HYPOPHOSPHITE OF LIME. $\text{CaO}, \text{PO}, 2\text{HO}$, may be obtained by carefully boiling phosphorus in thin cream of lime, filtering off the solution, and passing carbonic acid through it, to separate excess of lime. It is also formed by the action of boiling water on phosphuret of lime, and treating the clear liquor in the same way. The solution evaporated in vacuo, furnishes four-sided rectangular prismatic crystals of the hypophosphite, which are nearly equally soluble in hot and cold water, and quite insoluble in alcohol: they contain from 18 to 22 *per cent.* of water of crystallization. At a red heat in air they are converted into phosphate of lime, giving off phosphuretted hydrogen and water; $2[\text{CaO}, \text{PO}, 2\text{HO}] = 2\text{CaO}, \text{PO}_5, + \text{PH}_3 + \text{HO}$. This salt is useful for the preparation of a variety of other hypophosphites, which may be obtained by double decomposition. According to Wurtz, (*Ann. der Pharm.*, xliii. 322,) the crystals consist of

						Wurtz.	
Lime	1	...	28	...	32·32	...	33·06
Hypophosphorous acid.....	1	...	40	...	46·51	...	45·94
Water	2	...	18	...	21·17	...	21·00
<hr/>							
Crystallized hypophosphite of lime.....	1		86		100·00		100·00

PHOSPHITE OF LIME. When solutions of phosphite of ammonia and chloride of calcium are mixed, a white crystalline deposit is gradually formed, being a subphosphite; $2\text{CaO}, \text{PO}_3, 2\text{HO}$. (H. Rose, *Poggend.*, ix. 26.) When its aqueous solution is boiled, nacreous crystals of a more

basic phosphite are deposited, and a difficultly-crystallizable acid salt retained in solution. (DULONG.) An *acid phosphite of lime* may be obtained by the action of phosphorous acid on white marble: when the evolution of carbonic acid ceases, the liquor evaporated in vacuo yields acicular crystals, and if alcohol be added to their solution in water, neutral phosphite of lime falls, and an acid salt remains in solution; the composition of the acid phosphite of lime is, $\text{CaO}, \text{PHO}_4, \text{HO} + \text{HO}$. (WURTZ, *Ann. Ch. et Ph.*, Fevr., 1846.)

PHOSPHATE OF LIME. There appear to be several definite combinations of lime with phosphoric acid, among which the following have been particularly examined. (BERZELIUS, *Ann. Ch. et Ph.*, ii. 167. FUCHS. MITSCHERLICH, *Lehrb.* GRAHAM, *Elem.*)

1. COMMON PHOSPHATE OF LIME. TRIBASIC PHOSPHATE OF LIME. BONE-PHOSPHATE. $3\text{CaO}, \text{cPO}_5$. This salt occurs abundantly in bone-ash, and is found as a mineral product combined with fluoride of calcium, in *apatite* and *moroxite*. On adding chloride of calcium to the tribasic phosphate of soda, a corresponding phosphate of lime precipitates, the formula of which is $3\text{CaO}, \text{PO}_5$. (GRAHAM.) When a solution of bone-earth in hydrochloric or nitric acid is boiled to expel all carbonic acid, and precipitated by caustic ammonia, the pure bone-phosphate separates in the form of a bulky precipitate, which, when perfectly dried, is a white amorphous mass, composed of

						Fuchs.	Berzelius.
Lime	3	...	84	...	53.84	...	51.68
Phosphoric acid	1	...	72	...	46.16	...	48.32
<hr/>							
Tribasic bone phosphate	1		156		100.00	100.00	100.00

Berzelius represents bone-earth as a compound of 8 atoms of lime and 3 of phosphoric acid [$8\text{CaO}, 3\text{PO}_5$], or 50.9 lime + 49.1 phosphoric acid *per cent.*, and Graham, referring to this statement, observes, "that when moderately dried, the precipitated bone-earth retains 4 equivalents of water, and as it is a tribasic phosphate, its formula probably is $2[3\text{CaO}, \text{PO}_5] + \text{HO}, 2\text{CaO}, \text{PO}_5 + 3\text{HO}$." But the experiments of Fuchs and others show the identity of the above tribasic phosphate and bone-earth, and render the complex formula of Berzelius unnecessary.

When bone-phosphate is intensely heated with silica and charcoal it yields phosphorus and carbonic oxide. (See Wöhler's process, p. 413.) Digested in dilute sulphuric acid, this phosphate is resolved into sulphate of lime, and (if a sufficiency of sulphuric acid be used) phosphoric acid: thus 1 atom of bone-phosphate and 3 of oil of vitriol, yield 3 atoms of sulphate of lime and 1 of phosphoric acid; $3\text{CaO}, \text{PO}_5 + 3\text{SO}_3 = 3[\text{CaO}, \text{SO}_3] + \text{PO}_5$. If less sulphuric acid be used, an acid phosphate of lime is formed instead of free phosphoric acid; thus, 1 atom of bone-phosphate and 2 of sulphuric acid, yield sulphate of lime and monophosphate of lime; $3\text{CaO}, \text{PO}_5 + 2\text{SO}_3 = 2[\text{CaO}, \text{SO}_3] + \text{CaO}, \text{PO}_5$. (DÖBEREINER. BERZELIUS.) Hydrochloric and nitric acids readily dissolve bone-phosphate (abstracting 2 atoms of its lime and leaving CaO, PO_5 in solution?) Acetic acid, and water saturated with carbonic acid, also dissolve it. Caustic ammonia added to these acid solutions, throws down the original phosphate. It is

also slightly soluble in solutions of ammoniacal salts and of chloride of sodium: and when recently precipitated, it is slightly soluble in water. (R. PHILLIPS, *Ann. of Phil.*, xxii. 108.) Water containing starch or gelatine in solution, dissolves it somewhat more freely.

Native phosphate of lime (bone phosphate) occurs in the minerals called *apatite*, *moroxite*, *phosphorite* and *asparagus stone*; its primitive form is a six-sided prism: it also occurs in volcanic products; the former varieties phosphoresce when heated, but not the latter. Crystallized apatite is found of great beauty in Cornwall and Devon; the massive varieties are found at Schlackenwald, in Bohemia, and Estremadura, in Spain. (See DAUBENY, on the locality and composition of the Estremadura Phosphate, *Mem. Chem. Soc.*, ii. 97.) This is one of the most beautiful of the phosphorescent minerals. When fragments of it are placed upon iron heated just below redness, they shine with a brilliant pale green light. In these minerals the phosphate is generally associated with fluoride of calcium, the formula of apatite being $3[3\text{CaO}, \text{PO}_5] + \text{CaF}$. The substances known under the name of *coprolites*, and which appear to be the excrements of fossil reptiles, also abound in phosphate of lime. On the shore at Lyme Regis, and in the lias of the estuary of the Severn, they are singularly abundant, lying in some parts "like potatoes scattered upon the ground:" they occur in greater or less abundance throughout the lias of England, and in strata of all ages that contain the remains of carnivorous reptiles: in external form they resemble oblong pebbles, mostly from two to four inches in length, and one to two in diameter; but they vary in size with the calibre of the intestines which have produced them: their usual color is ash-grey interspersed with black; their texture resembles indurated clay, having a conchoidal and glossy fracture: the scales and occasionally the teeth and bones of fishes are irregularly dispersed through them. (BUCKLAND, *Bridgwater Treatise*; and *Trans. Geol. Soc.*, 1829.) Phosphate of lime is found in small quantities in some varieties of chalk, and in certain schists, and other rocks, and its presence in all fertile soils, and in the vegetables they produce, and through which it is conveyed to the animals that feed upon them, are circumstances bearing most importantly upon agriculture, and which give great interest to the economy of bone manure, and other sources of the phosphates. Minute quantities of phosphate of lime and phosphate of iron have been detected by Graham in the water of the deep wells of London; he was led to look for it from the rapid growth of confervæ, and supposes that the superiority of certain waters for irrigation may depend upon the presence of phosphoric acid. From 100 parts of the residue of the evaporation of the water of a deep well near Long acre, he obtained 53 sulphate of soda, 22 chloride of sodium, 11 carbonate of soda, 11 carbonate of lime, 2 carbonate of magnesia, 1 silica, 0.43 phosphate of iron, 0.34 phosphate of lime. (*Mem. Ch. Soc.*, May, 1845.)

2. TRIBASIC DIPHOSPHATE OF LIME AND WATER. $2\text{CaO}, \text{HO}, \text{PO}_5 + 3\text{HO}$. When solution of common phosphate of soda is added drop by drop to a solution of chloride of calcium, this compound is formed, in small opaque acicular crystals: [if excess of the phosphate of soda be added, the precipitate gives phosphoric acid to the soda salt, and becomes

bone-earth phosphate.] It is insoluble in water, but very soluble in dilute acids: held in solution by carbonic acid, it is occasionally found in mineral waters. (BERZELIUS.) It consists of

							Berzelius.
Lime	2	...	56	...	34.15	...	35.42
Phosphoric acid	1	...	72	...	43.90	...	41.90
Water (basic)	1	...	9	...	5.48	}	22.68
Water of crystallization	3	...	27	...	16.47		
<hr/>							
Crystallized tribasic diphosphate of lime and water	}	1	164		100.00		100.00

A phosphate of lime = $2\text{CaO}, \text{HO}, \text{PO}_5 + 5\text{HO}$, is described by Dr. Percy (*Mem. Ch. Soc.*, II. 222), as obtained by adding a solution of chloride of calcium to a dilute solution of common phosphate of soda, till precipitation ceases, then passing carbonic acid, for about an hour, through the mixture, filtering, and setting aside. In a day or two white scaly crystals (rhomboidal plates) are deposited, having the above formula. All their water is expelled by a red heat.

3. PYROPHOSPHATE OF LIME. BIBASIC PHOSPHATE OF LIME. $2\text{CaO}, 6\text{PO}_5$. This salt is probably produced by heating the preceding to redness, when it parts with the whole of its water, and leaves an anhydrous bibasic phosphate.

4. METAPHOSPHATE OF LIME. MONOBASIC PHOSPHATE. $\text{CaO}, a\text{PO}_5$. When a solution of any one of the preceding salts in phosphoric, hydrochloric, or nitric acids is evaporated, small sour and deliquescent crystals are deposited, which, when heated to redness, give off water and leave an insoluble vitreous monophosphate: the same salt results as above stated from the action of 2 atoms of oil of vitriol upon 1 of bone phosphate. It consists of

Lime	1	...	28
Phosphoric acid	1	...	72
<hr/>			
Metaphosphate of lime	1		100

Hydrated metaphosphate of lime is thrown down in the form of a transparent viscid precipitate when metaphosphate of soda is added to chloride of calcium. (GRAHAM.)

CALCIUM AND SELENIUM. *Protoseleniuret of calcium* is obtained by heating perseleniuret to redness: it is of a reddish color, insoluble and tasteless: the same compound is thrown down in the form of a flesh-red precipitate when solutions of chloride of calcium and seleniuret of potassium are mixed. *Perseleniuret of calcium* (mixed with selenite of lime) is formed when a mixture of selenium and lime is heated nearly to redness: a dark brown insipid, inodorous, insoluble substance results, from which acids separate selenium in a red flocculent form. (BERZELIUS, *Lehrbuch*.)

SELENITE OF LIME. Berzelius has described a *neutral selenite* and a *biselenite of lime*. The former gradually falls in a pulverulent form, from a solution obtained by the action of selenious acid on carbonate of lime. If fused at a red heat in a glass vessel, it corrodes and passes

through it. When dissolved in selenious acid small prismatic crystals of *biselenite of lime* are obtained, which are permanent in the air: when heated, or digested in ammonia, they lose acid, and become neutral. (*Ann. Ch. et Ph.*, ix. 263.)

SELENIATE OF LIME has not been examined.

CARBONATE OF LIME, CaO, CO_2 , is the most abundant compound of this earth; it exists in river and spring water, and, consequently, in the ocean, and is an essential ingredient in fertile soils: when lime-water is exposed to air, it becomes gradually covered with an insoluble film of carbonate of lime: hence its use as a test of the presence of carbonic acid; but excess of carbonic acid redissolves it, producing a supercarbonate. It follows, therefore, that if lime-water be added in equivalent proportion to water holding carbonate of lime in solution by excess of carbonic acid, the whole of the lime may be thrown down in the form of an insoluble carbonate, and the water will remain pure. Upon this principle Professor Clark, of Aberdeen, proposes to render waters which are hard and unfit for domestic use in consequence of the carbonate of lime dissolved in them by excess of carbonic acid, soft and pure by the due addition of lime or lime-water: he has patented this process, which, however, is scarcely practically applicable. "What occurs in this operation," he observes, "will be understood if we suppose that one pound of chalk, after being burned to nine ounces of caustic lime, is dissolved, so as to form forty gallons of lime-water; that another pound is dissolved by seven ounces of extra carbonic acid, so as to form 500 gallons of a solution of bicarbonate of lime; and that the two solutions are mixed, making up together 540 gallons. The nine ounces of caustic lime from the one pound of chalk unites with the seven extra ounces of carbonic acid that hold the other pound of chalk in solution. These nine ounces of caustic lime and seven ounces of carbonic acid form sixteen ounces, that is, one pound of chalk, which being insoluble in water, becomes visible, at the same time that the other pound of chalk, being deprived of the extra seven ounces of carbonic acid that kept it in solution, reappears. Both pounds of chalk will be found at the bottom after subsidence. The 540 gallons of water will remain above, clear and colorless, without holding in solution any sensible quantity either of caustic lime or of bicarbonate of lime." Carbonate of lime is also precipitated by the carbonated alkalis from solutions of calcareous salts. It is a tasteless white powder, insoluble in pure water (or, according to Bucholz, soluble in 16000 parts of pure water?) and having no alkaline reaction. Exposed for a sufficient time to the joint action of a red heat and a current of air, the whole of the carbonic acid escapes, to the amount of 44 *per cent.* and quick-lime is obtained. Hence carbonate of lime consists of

	Erdmann and											
	Kirwan.			Marcet.			Stromeyer.			Berzelius.		
	Marchand.											
Lime	1....	28	...	56	...	55	...	56.1	...	56.35	...	56.4
Carbonic acid ...	1....	22	...	44	...	45	...	43.9	...	43.65	...	43.6
Carbonate of lime	1	50		100		100		100.0		100.00		100.0

Mr. Daniell obtained crystals of carbonate of lime from a solution of lime in syrup. When a solution obtained by boiling together 1 part of

hydrate of lime, 3 of sugar, and 6 of water, was filtered and exposed for fifteen days to the air, Gay Lussac found the whole of the lime deposited in acute rhombic crystals, consisting of 1 atom of carbonate of lime and 5 of water. In this case, the carbonic acid is derived from the atmosphere. These crystals are not changed by cold water, but in hot water, or exposed to air, they gradually fall to powder. Boiled in alcohol they retain their form, but lose 2 atoms of water, becoming $\text{CaO}, \text{CO}_2, 3\text{HO}$. (*Ann. Ch. et Ph.*, XLVIII. 301.) What is termed *cream of lime* gradually absorbs carbonic acid to the amount of half an equivalent, when exposed to the air, and forms a definite compound of hydrate and carbonate. In an atmosphere of carbonic acid it rapidly combines with half an equivalent of carbonic acid, but does not acquire three-fourths of an equivalent by 2 or 3 weeks' exposure to such an atmosphere. (GRAHAM.) It also appears that in burning lime one half of the carbonic acid escapes more easily than the other, indicating the existence of a dicarbonate $= 2\text{CaO}, \text{CO}_2$. (FUCHS, *Poggend.*, XXVII. 601.)

Native Carbonate of Lime occurs in great abundance and in various forms. The primitive form of crystallized carbonate of lime, or *calcareous spar*, is an obtuse rhomboid of $105^\circ 5'$ and $74^\circ 55'$ (WOLLASTON), $101^\circ 59'$ and $78^\circ 50'$ (DUMAS). Its specific gravity is 2.72. It occurs in every kind of rock, and its secondary forms are more numerous than those of any other substance. Bournon, in his *Traité de Minéralogie*, has described and figured six hundred and eighty modifications. What is termed *Iceland spar* is this substance, in its primitive form, and of extreme purity*: it is highly doubly refractive (p. 94) when transparent; some of the varieties are opaque or translucent, snow-white, or tinged of different hues. The mineral is recognised by its foliated and rhomboidal fracture and its moderate hardness, being scratched by fluor-spar; before the blow-pipe it loses carbonic acid, and becoming *lime*, is intensely luminous; it dissolves with effervescence in hydrochloric acid, and the solution, when much diluted, affords a white precipitate with oxalate of ammonia. Carbonate of lime sometimes forms *stalactites* and *stalagmites* (from *σταλαζω*, I drop, and *σταλαγμα*, a drop), of which some of the caverns of Derbyshire furnish magnificent specimens; it is there deposited from its solution in water acidulated by carbonic acid, and substances immersed in this water become incrustated by carbonate of lime when the excess of acid flies off, as seen in the *petrifying-well* at Matlock. A fibrous carbonate of lime, called *satin-spar*, is found in Cumberland.

A peculiar variety of carbonate of lime, originally found in Arragon, in Spain, has been termed *Arragonite*; it often occurs in six-sided crystals of a reddish color, and harder than the common carbonate. There is an acicular or fibrous variety, found in France and Germany; and the white radiated substance, improperly called *flos ferri*, is also regarded as of the

* Erdmann and Marchand, in a paper on the atomic weights of hydrogen and calcium, have shown them, as already stated, to be 1 and 20, the composition of pure carbonate of lime being accurately 56 lime, 44 carbonic acid. (*Ann. Ch. et Ph.*, Juin, 1843.) The following is their analysis of Iceland spar:

Carbonate of lime	99.961
Silica	0.014
Magnesia.....	0.005
Oxide of iron	0.020
Potassa or soda	traces
Sulphuric acid, chlorine, fluorine	0.000
	<hr/>
	100.000

same species. Some varieties contain about 3 *per cent.* of strontia. The crystalline forms of Arragonite have been described in detail by Bournon (*Traité de Minéralogie*); the primary form is a right rhomboidal prism of $116^{\circ} 10'$ (BROOKE). The crystals contain a little water, which they lose when heated, and crumble into powder, by which Arragonite is distinguished from calcareous spar. It is also heavier, its specific gravity being from 2·8 to 2·9.

All the varieties of *marble* and *limestone* consist essentially of carbonate of lime; of these, *white granular limestone*, or *primitive marble*, is most esteemed; there are, also, many colored varieties of extreme beauty. It is distinguished from *secondary limestone* by the absence of organic remains, by its granularly foliated structure, and by its association with other primitive substances. The most celebrated statuary marble is that of Paros and Mons Pentelicus near Athens; of these, some of the finest specimens of ancient sculpture are composed. The marble of Carrara, or Luni, on the eastern coast of the Gulf of Genoa, is also much esteemed; it is milk-white and less crystalline than the Parian.

Many beautiful secondary marbles for ornamental purposes are quarried in Derbyshire, and especially the *black marble*, called also *Lucullite*, from the admiration bestowed on it by Lucius Lucullus. (PLINY, *Hist. Nat.*, xxxvi. 8.) Its color appears to depend upon a small quantity of carbonaceous matter. Westmoreland and Devonshire also afford beautiful varieties of ornamental marble; and in Anglesea, a marble intermixed with green serpentine is found, little inferior in beauty to the *verd antique*.

Among the inferior limestones, we enumerate many varieties, such as *common marble*; *bituminous limestone*, abundant upon the Avon, near Bristol, and known under the name of *swine-stone* or *stink-stone*, from the peculiar smell which it affords when rubbed; *Oolite* or *Roestone*, of which the houses of Bath are built; and its variety, called *Portland-stone*; *Pisolite*, or *peastone*, consisting of small rounded masses, composed of concentric layers, with a grain of sand in the centre; and lastly *chalk** and *marl*.

All these substances are more or less employed for ornamental or useful

* The chalk of the Brighton Cliffs, and probably elsewhere, contains about 0·1 *per cent.* of phosphate of lime; the following is its analysis, by Dr. Schweitzer. (*Mem. Ch. Soc.*, Apr. 1842):

Carbonate of lime.....	98·57
„ of magnesia.....	0·38
Phosphate of lime.....	0·11
Protoxide of iron	0·08
„ of manganese	0·06
Alumina	0·16
Silica.....	0·64
	100·00

“To ascertain the quantity of phosphoric acid, I followed Dr. Schulze’s method (*Journal für pratk. Chemie*, xxi. S. 387-389), which he recommends for the analytical investigation of soils. The process is based upon the fact, that phosphate

of lime and phosphate of magnesia are soluble in acetic acid, while the phosphate of peroxide of iron and phosphate of alumina are not so. This being the case, the soil or mineral is to be treated with hydrochloric acid, and the iron which the solution contains peroxidised, (the phosphate of *protoxide* of iron being soluble in acetic acid.) Should the muriatic solution contain more phosphoric acid than oxide of iron or alumina, (which seldom is the case, as the latter are usually predominant,) peroxide of iron or alumina is to be added, the solution must also be freed from every trace of silica. The earthy muriates are precipitated with ammonia, after which acetic acid is added, and the whole gently digested. The precipitate will dissolve again, with the exception of the phosphates of peroxide of iron and alumina. When both these in-

purposes; they afford *quick-lime* when burned, and in that state are of great importance in agriculture, and as ingredients in the cements used for building. There is a great variety of limestones used for burning into quick-lime, and, generally speaking, any of the varieties may be employed which neither fuse nor crumble into powder at the temperature required to expel the carbonic acid, which is a full red-heat.

Lime-burning. Although all the species of limestone may, by burning, be brought to the state of quick-lime, the substances belonging to the family of *compact* limestone are the only ones that are employed for this purpose in the large way. Sometimes calcareous spar, and statuary marble, are used in the laboratory for the purpose of procuring a lime purer than ordinary. But owing to the crystalline texture of these substances, the laminae of which they are composed part from each other during the escape of the carbonic acid, so that by the time they are rendered caustic, their cohesion is destroyed, and they are reduced to the state of sand, a circumstance which must always prevent them from being used in kilns of the common construction. The lime-kiln at present almost universally employed in this country, is a cup-shaped concavity, in a solid mass of masonry, open at top and terminated at bottom by a grate, immediately above which is an iron door. This simple furnace is first charged with fuel, (either wood, or coal and cinders, but more commonly the latter,) upon which is afterwards laid a stratum about a foot thick of limestone, broken into pieces not larger than the fist; to this succeeds a charge of fuel; and so on alternately, keeping the kiln always full. The pieces of limestone descend towards the bottom of the kiln in proportion as the fuel is consumed, being in the mean time kept at a pretty full red-heat. At this temperature, the water and carbonic acid are driven off; and by the time the limestone arrives at the bottom of the kiln, which happens in about forty-eight hours, it is rendered perfectly caustic. The door above the grate is then opened, and the lime below the next descending stratum of fuel is raked out; the remaining contents of the furnace sink down, and a fresh charge is laid on the top. The compact limestone, after having undergone this process, though much lighter and more porous than before, still retains its figure unaltered; hence it is readily separable from the ashes of the fuel, and is sufficiently hard to be carried from place to place without falling to pieces. (AIKIN'S *Dictionary*, Art. LIME; URE'S *Dictionary of Arts*, and DUMAS, *Chimie app. aux Arts*, ii. 481; and in reference to the use of argillaceous limestones for cements and mortar, see VICAT, *Recherches experimentales*, Paris, 1818, and *Ann. Ch. et Ph.*, 3rd Series, ii. 426.)

Attempts have been made to burn lime, or, in other words, to expel the carbonic acid from limestone, in close vessels, but the carbonic acid

gredients enter into the precipitate, caustic potassa will give the means of ascertaining their respective quantities."

"The solubility of the phosphate of protoxide of iron, and the insolubility of peroxide of iron, in acetic acid, when freshly precipitated, give an excellent method to separate quantitatively these two degrees of oxidation. The manipulation is obvious,

"The discovery by Professor Ehrenberg, that the Brighton chalk consists of microscopic shells, is a decided proof of its animal origin, to which may now be added an additional one, viz., the presence of phosphate of lime, which is a usual, although secondary ingredient of the shells of Crustaceæ."

cannot, under such circumstances, be driven off; and, indeed, Bucholz found, that upon strongly heating five or six pounds of pure chalk, closely pressed into a crucible, and out of the access of air and its watery vapor, scarcely any carbonic acid was driven off; but, with the exception of a small portion upon the surface, the contents of the crucible were converted into a hard, foliated, yellowish mass, retaining nearly the whole of the carbonic acid, semi-transparent, and evidently having undergone incipient fusion. (GEHLEN'S *Jour.*, Second Series, i. 271.) This agrees with Sir James Hall's experiments, who, by exposing powdered chalk to great heat and pressure, succeeded in fusing it (without escape of carbonic acid), and thus imitating the process of nature, by which he supposes *marble* to have been formed. (*Phil. Trans. Edinb.*, vol. vi.)

CARBONATE OF LIME AND SODA. A mineral named *Gay Lussite* contains 1 atom of carbonate of lime, 1 of carbonate of soda, 5 water. (BOUSSINGAULT, *Ann. Ch. et Ph.*, April, 1843.)

CYANIDE OF CALCIUM has not been obtained. When hydrate of lime is digested in hydrocyanic acid, a solution of hydrocyanate of lime is formed, which upon evaporation is resolved into ammonia and carbonate of lime.

SULPHOCYANIDE OF CALCIUM forms deliquescent acicular crystals, soluble in water and in alcohol.

MELLONIDE OF CALCIUM is soluble in boiling water, and separates as the solution cools in acicular crystals, containing 24 *per cent.* of water. (LIEBIG.)

BORATE OF LIME is a white tasteless powder of very difficult solubility in water. At a red heat it forms a vitreous mass. According to Tünnermann (GMELIN, *Handbuch*), the precipitate formed on adding a solution of borax to nitrate of lime, is a monohydrated biborate, = CaO , 2BO_3 , HO , the anhydrous salt consisting of

						Tünnermann.	
Lime	1	...	28	...	28.56	...	30.17
Boracic acid	2	...	70	...	71.44	...	69.83
<hr/>							
Biborate of lime	1		98		100.00		100.00

FLUOBORATE OF LIME forms a gelatinous mass, which has an acid taste and reddens litmus. Water, especially boiling, resolves it into a basic and acid salt. (BERZELIUS.)

CHARACTERS OF THE SALTS OF LIME. These salts have the following properties: those which are *soluble* in water are not altered by pure ammonia, but they are decomposed by potassa and soda, which throw down hydrate of lime. They are also decomposed by the carbonates of potassa, soda, and ammonia, which produce precipitates of *carbonate of lime*. Oxalate of ammonia produces in their solutions a white precipitate of *oxalate of lime*, which, exposed to a red-heat, affords carbonate of lime or pure lime. It is soluble in nitric and hydrochloric acids, but scarcely soluble in acetic acid. This test will detect 1 part of lime in most of the

salts of lime, in 50000 of water, and even after a time, an opalescence ensues where the amount of lime does not exceed 100,000th. The soluble sulphates throw down sulphate of lime from such solutions of the salts of lime as are not very dilute. Ferrocyanide of potassium does not affect dilute solutions of the salts of lime, but when very concentrated, they give after some time a white flocculent deposit. Such of the salts as are soluble in alcohol, tinge the edge of its flame of a reddish color, somewhat like the tint given by the salts of strontia. Those salts of lime which are *insoluble* in water, are decomposed by being boiled with carbonate of potassa, and afford *carbonate of lime*: they are mostly readily soluble in nitric and hydrochloric acids.

§ V. BARIUM. Ba. 69.

THIS metal was discovered by Davy, in 1808; he obtained it by placing a globule of mercury upon moistened *baryta*, lying upon a plate of platinum in connexion with the positive pole of a powerful Voltaic battery: the negative wire was then brought into contact with the mercury, which, combining with the evolved barium, gradually became an *amalgam*; this was heated out of the contact of air so as to distil off the mercury, and the barium remained. Barium may also be procured by passing potassium in vapor over *baryta* heated to redness in an iron tube, and afterwards withdrawing the reduced barium, which the residue contains, by means of mercury; the latter metal is separated by distillation in a retort, care being taken not to raise the temperature to redness, for then the barium decomposes glass. (GRAHAM.)

Barium has a specific gravity above 2. It is of an iron-grey color, and rapidly absorbs oxygen; when gently heated, it burns with a red light; it decomposes water, evolving hydrogen, and forming a solution of *baryta*; its properties, however, have hitherto not been accurately ascertained. Its equivalent is 69. (68·6 GMELIN, 68·7 BERZELIUS and TURNER.)

OXIDE OF BARIUM. BARYTA. BaO , is obtained by exposing pure *nitrate of baryta* for some time to a bright red-heat in a porcelain retort or covered crucible; it acts upon platinum, and if a silver crucible be employed, the heat required for the perfect decomposition of the nitrate is such as to endanger its fusion. *Baryta* may also be obtained by subjecting artificial *carbonate of baryta* (which see) to an intense white heat, thoroughly mixed with about 10 *per cent.* of finely-powdered charcoal, in a plumbago crucible.

Graham uses *iodate of baryta* as a source of pure *baryta*: it may be fused in a porcelain retort, and is more easily decomposed than the nitrate; it has not the troublesome property of fusing and swelling up when heated, which the latter salt possesses. The iodine comes off with the oxygen, and may be recovered. (See *iodate of baryta*.)

Baryta is generally in the form of a porous mass, or grey powder, and when pure, is very difficult of fusion. Its specific gravity is about 4, hence the name *Baryta*, as being the *heaviest* of the substances usually called *earths* (from $\beta\alpha\rho\upsilon\varsigma$, *heavy*). It has a strong alkaline taste, and reaction on vegetable colors. It is insoluble in alcohol. It eagerly absorbs water, heat is evolved, and a white hydrate is formed. After long exposure to

air it becomes white, and is a mixture of the hydrate and carbonate. Baryta, considered as a *protoxide of barium*, consists of

						Davy.	Berzelius.
Barium	1	69	89·6	89·55
Oxygen	1	8	10·4	10·45
<hr/>							
Baryta	1		77		100·0		100·00

HYDRATE OF BARYTA. BaO, HO . When pure baryta is sprinkled with water it absorbs it, becomes intensely hot, and even, according to Barry, incandescent, (*Ann. of Phil.*, 2nd Series, ii. 77,) and crumbles down into a bulky white powder, which fuses, but does not give out water at a red heat. It is composed of

Baryta	1	77	89·53
Water	1	9	10·47
<hr/>					
Hydrate of baryta	1		86		100·00

Hydrate of baryta dissolves in 20 parts of cold, and in 3 of boiling, water (DAVY), forming a solution which is a very delicate test of the presence of carbonic acid, and which speedily becomes covered with a film of carbonate of baryta when exposed to air. A saturated solution of baryta in hot water, deposits flattened hexagonal prisms as it cools, containing, according to Dalton, 20, but according to Phillips, 10, equivalents of water. (*Phil. Mag.*, vi. 52, 3rd Series.) According to Smith (*Phil. Mag.*, and *Annals*, vi. 53, and ix. 87), this hydrate contains 9 atoms of water, 7 of which it loses when dried upon a sand-bath, and retains 2; of these 1 is expelled at a red-heat, and 1 retained, forming the above protohydrate. According to Filhol, the crystals of hydrate of baryta, dried in blotting paper at common temperature, contain 48·6 *per cent.* of water = 8 equivalents. (*Journ. de Pharm.*, 1845.) *Baryta-water* is powerfully alkaline and poisonous: but when in contact of carbonic acid, it becomes covered with successive films of insoluble carbonate, so that at length pure water only remains.

PEROXIDE OF BARIUM. BaO_2 . This compound is obtained when baryta is heated in oxygen, or when dry oxygen gas is passed over fragments of baryta heated to dull redness in a glass or porcelain tube: it may also be formed by adding 1 part of chlorate of potassa to 4 of baryta, previously heated to redness in a platinum crucible; the oxygen of the chlorate combines with the baryta, and, by the action of cold water, the remaining chloride of potassium may be washed out, and a *hydrated peroxide of barium* remains, composed of 1 equivalent of baryta, 2 of oxygen, and 6 of water, which admits of being dried at common temperatures. (WÖHLER and LIEBIG.) The application of this compound to the production of the *peroxide of hydrogen*, or *oxygenated water*, has already been pointed out (p. 312). When the anhydrous peroxide, which is of a grey color, is put into cold water, it does not evolve heat, but becomes a white, pulverulent, and insoluble hydrate, $\text{BaO}_2, 6\text{HO}$; but if this be boiled in water, it then gives out an equivalent of oxygen, and reverts to the state of protoxide, which is soluble. When peroxide of barium is heated in hydrogen it becomes incandescent, emitting a greenish flame, and absorbing the gas; protohydrate of baryta is the product.

CHLORIDE OF BARIUM. BaCl . This compound may be obtained by heating baryta in chlorine, in which case oxygen is evolved, to the amount of half a volume for every volume of chlorine absorbed; or in hydrochloric acid gas, when it becomes red-hot, and chloride of barium and water are the results. It is generally formed by dissolving carbonate of baryta in diluted hydrochloric acid, evaporating to dryness, and fusing the residue in a covered platinum crucible. It may also be produced by exposing a mixture of equal parts of powdered sulphate of baryta and chloride of calcium to a red-heat for an hour, in a covered Hessian crucible; the salts fuse and mutually decompose each other: when the crucible has cooled, its contents are powdered, put into boiling water, well stirred together, and filtered as rapidly as possible, otherwise sulphate of baryta would be recomposed; on evaporating the filtered liquid crystals of chloride of barium are obtained, whilst the undecomposed chloride of calcium remains in solution. (DUMAS.)

Chloride of barium, after it has been fused at a red-heat, is translucent and of a greyish color; sp. gr. 3·8; its taste is acrid; it is not deliquescent, but it absorbs aërial moisture and becomes opaque, increasing in weight after a few days to the amount of 13 to 14 *per cent.*: when moistened it evolves heat: 100 parts of water at 32° dissolve between 32 and 33 parts of this anhydrous chloride: it is insoluble in absolute alcohol, (said to be soluble in 400 parts of anhydrous alcohol; GRAHAM.) It is generally kept in aqueous solution, (*muriate of baryta*), and is in constant use in the laboratory as a test and precipitant for sulphuric acid: this solution yields, when evaporated, flat four-sided crystals, sp. gr. 3·049, bevelled at their edges, and permanent in ordinary states of the atmosphere, but efflorescent, from the loss of water of crystallization, in a very dry air at 60° . At 212° the water is soon expelled, and anhydrous chloride remains. 100 parts of water at 60° dissolve about 43 parts of these crystals, and at 222° , which is the boiling-point of the saturated solution, 100 of water dissolve 78. The anhydrous chloride of barium consists of

							Turner.
Barium	1	69	65·7	65·984
Chlorine.....	1	36	34·3	34·016
<hr/>							<hr/>
Chloride of barium	1		105		100·0		100·000

The crystals contain, according to Phillips, 14·5 *per cent.* of water (*Ann. of Phil.*, N.S., vi. 342). As sold by chemists, their solution often gives a precipitate with pure ammonia owing to the presence of chloride of lead. (A. TAYLOR.) The composition of the crystals is

							Pleischl.	J. Davy.
Chloride of barium	1	105	85·36	84·3 83·91
Water	2	18	14·64	15·7 16·09
<hr/>							<hr/>	<hr/>
Crystals of hydrated chloride of barium	1		123		100·00		100·0	100·00

CHLORATE OF BARYTA. BaO, ClO_5 , was formed by Chenevix in the same way as chlorate of potassa, namely, by passing chlorine through an aqueous solution of baryta; but in consequence of the similar solubility of chloride of barium and chlorate of baryta, considerable difficulty attended the separation of the products. It was effected by adding to the solution of the mixed salts, a solution of phosphate of silver in acetic

acid, by which the chloride of barium was decomposed, and chloride of silver and phosphate of baryta were formed, both of which are insoluble. Chlorate of baryta may also be obtained by saturating aqueous chloric acid with hydrate or carbonate of baryta: or it may be formed, as suggested by Wheeler, by adding a hot solution of chlorate of potassa to a solution of silicated hydrofluoric acid; the potassa is precipitated in the form of an insoluble silicofluoride of potassium, and the chloric acid remains in solution, and may be saturated with carbonate of baryta, which throws down any excess of the silicated fluoric acid, and leaves chlorate of baryta in solution, from which the salt may be obtained by evaporation.

Chlorate of baryta forms rhombic prisms, soluble in about 4 parts of water at 60° , and nearly insoluble in alcohol; they contain 2 equivalents of water = 10 *per cent.* (CHENEVIX), which is evolved at 248° ; at 482° they begin to give off oxygen, and fuse at 752° , giving off all their oxygen and a trace of chlorine: heated rapidly the salt is suddenly decomposed with detonation. (WAECHTER.) Sprinkled with sulphuric acid it becomes luminous. It is decomposed by dilute sulphuric acid, furnishing sulphate of baryta and chloric acid, and is the readiest source of that acid (p. 284). The anhydrous salt consists of

						Chenevix.	
Baryta	1	...	77	...	50.3	...	47.3
Chloric acid	1	...	76	...	49.7	...	52.7
<hr/>						<hr/>	
Chlorate of baryta	1		153		100.0		100.0

PERCHLORATE OF BARYTA. BaO, ClO_7 , formed by saturating aqueous perchloric acid with baryta, forms long prismatic crystals, deliquescent, and soluble in water and in alcohol. (SERULLAS, *Ann. Ch. et Ph.*, XLVI. 303.)

IODIDE OF BARIUM. BaI , is formed by acting upon baryta, or carbonate of baryta, by hydriodic acid, evaporating the solution, and heating the residue. It may also be formed by passing hydriodic acid gas over baryta; the action is very intense, and it is stated by Dumas, that even when the gas is cooled down to 0° the baryta becomes incandescent: the baryta and the acid are of course mutually decomposed, and water and iodide of barium are the products.

Iodide of barium may be obtained in acicular (hydrated) crystals; it is very soluble in water and alcohol, somewhat deliquescent, and when exposed to the air carbonate of baryta is formed and a portion of iodine set free. It is not fusible at a red heat, and if a current of oxygen be then directed upon it the vapor of iodine appears and it becomes alkaline, whence it may be inferred that the affinity of barium for oxygen is greater than for iodine. (DUMAS.) It consists of

Barium	1	...	69	...	35.4
Iodine	1	...	126	...	64.6
<hr/>					
Iodide of barium	1		195		100.0

IODATE OF BARYTA. BaO, IO_5 . When iodine is added to baryta-water, iodide of barium and iodate of baryta are the results; the latter salt, in consequence of its little solubility, falls in the form of a white hydrated precipitate, which may be purified by washing it upon the filter.

It is also formed by double decomposition when iodate of potassa or soda is added to a soluble barytic salt. According to Millon, (*Ann. Ch. et Ph.*, ix. 416,) it is best formed by boiling caustic baryta in excess of iodic acid, and washing with hot water: it remains as a white crystalline powder, containing an equivalent of water. Grosourdy (*Jour. Ch. Med.*, 1843, p. 373,) recommends mixing iodine with solution of chloride of barium and passing chlorine into it, till the whole is converted into iodate of baryta: if the object be to obtain iodic acid, the iodate may be decomposed by its equivalent of sulphuric acid. If iodate of baryta be used as a source of pure baryta it requires to be prepared in large quantities, and the following process is recommended by Graham (*Elem. Chem.*): Two ounces of iodine are diffused through a pint of water and chlorine passed through it till dissolved; carbonate of soda is then added to the acid liquor till it is slightly alkaline, when a large precipitation of iodine occurs, which may be separated on a filter, and treated as before. The filtered solution contains iodate of soda and chloride of sodium with a trace of carbonate, which may be neutralized with hydrochloric acid. On afterwards adding chloride of barium to the filtered solution so long as a precipitate is produced, the whole of the iodic acid will be thrown down as iodate of baryta, which may be collected on a filter and dried.

This salt may be rendered anhydrous by exposure to a heat of about 390° ; at a red-heat it evolves oxygen and some iodine, and leaves a subperiodate. It is deposited in crystals from its solution in hot nitric acid. At 62° it requires more than 3000 parts of water for its solution; and at 212° about 600 parts. (GAY LUSSAC, *Ann. Ch. et Ph.*, xci. 81.) It consists of

				Rammelsberg.			
Baryta	1	77	31.7	Baryta	1	77	30.55
Iodic acid.....	1	166	68.3	Iodic acid	1	166	65.50
				Water	1	9	3.95
<hr/>				<hr/>			
Anhydrous iodate } of baryta	1	243	100.0	Crystallized iodate } of baryta	1	252	100.00

PERIODATE OF BARYTA. BaO, IO_7 , is formed by heating a mixture of iodide and peroxide of barium. The *subperiodate*, obtained by heating the iodate to redness, contains 5 atoms of baryta and 1 of periodic acid = $5\text{BaO}, \text{IO}_7$. This salt, dissolved in nitric acid and precipitated by ammonia, yields a yellow powder, insoluble in water, but easily soluble in nitric acid, containing 5 atoms of baryta and 2 of periodic acid = $5\text{BaO}, 2\text{IO}_7$. (RAMMELSBERG, *Poggend.*, xlv. 572. BENCKISER, *Ann. der Pharm.*, xvii. 254. GMELIN, *Handbuch*.)

BROMIDE OF BARIUM. BaBr , is obtained by saturating hydrobromic acid with baryta and evaporating to dryness; or a solution of sulphuret of barium may be decomposed by hydrobromic acid; it is fusible, soluble in water and in alcohol, and crystallizes in opaque mammellated masses; or, according to Henry, Jun., in white rhombic prisms, isomorphous with chloride of barium, and containing 1 atom of water. The anhydrous bromide consists of

Barium.....	1	69	46.9
Bromine	1	78	53.1
<hr/>			
Bromide of barium	1	147	100.0

The solubility of bromide of barium in absolute alcohol, affords a means of separating it from chloride of barium, which is insoluble in it, or at least very nearly so.

BROMATE OF BARYTA. BaO, BrO_5 . When excess of bromine is added to baryta-water, bromate of baryta is precipitated, and bromide of barium remains in solution. $6\text{BaO} + 6\text{Br} = 5\text{BaBr} + \text{BaO}, \text{BrO}_5$. Or, a strong solution of chloride of barium may be decomposed by bromate of potassa, in which case, $\text{BaCl} + \text{KO}, \text{BrO}_5 = \text{BaO}, \text{BrO}_5 + \text{KCl}$. Bromate of baryta crystallizes in small rectangular prisms, soluble in 130 of cold, and in 24 of boiling water. The crystals ($\text{BaO}, \text{BrO}_5, \text{HO}$) require to be heated nearly to 400° before they lose the whole of their water, and the residue when highly heated deflagrates into oxygen and bromide of barium without any intermediate formation of a perbromate.

Baryta	1....	77....	39·5	Baryta	1....	77....	37·74....	37·56
Bromic acid	1....	118....	60·5	Bromic acid	1....	118....	57·84....	58·03
				Water	1....	9....	4·42....	4·41
<hr/>				<hr/>				
Anhydrous bromate of baryta	}	1	195	100·0	Crystallized bromate of baryta	}	1	204
							100·00	100·00

FLUORIDE OF BARIUM. BaF , is best obtained by adding fresh precipitated and moist carbonate of baryta to hydrofluoric acid; carbonic acid is expelled, and the fluoride remains in the form of a white powder, very sparingly soluble in water, but soluble in hydrochloric and nitric acids. It combines with fluoride of boron, forming prismatic hydrated crystals $= \text{BaF}, \text{BF}_3, 2\text{HO}$. (BERZELIUS.)

HYPONITRITE OF BARYTA. A salt having the formula $\text{BaO}, \text{NO}_3, \text{HO}$ is described by Fritzsche, (*Poggend.* xix. 179;) it is obtained by cautiously heating the nitrate, dissolving the residue in water, and crystallizing; or by passing nitrous acid vapor into baryta-water, evaporating to dryness, and acting on the residue by a small quantity of water, which dissolves the more soluble hyponitrite: its crystals are said to resemble those of the nitrate. According to Hess, the salt resulting from the ignition of nitrate of baryta, contains nitric oxide; he represents it as $= \text{BaO}, \text{NO}_2 + 2\text{HO}$.

NITRATE OF BARYTA. BaO, NO_5 , may be produced by dissolving the native carbonate in dilute nitric acid, evaporating to dryness, redissolving and crystallizing; or by decomposing a solution of sulphuret of barium by dilute nitric acid. It forms permanent octohedral and cubo-octohedral crystals, which are anhydrous: their forms have been described by Brooke. (*Ann. of Phil.*, N. S., vii. 21.) The taste of this salt is acrid and astringent. It is soluble in 12 parts of cold and 4 of boiling water; or, according to Gay Lussac, 100 parts of water, at 32° , dissolve 5 parts; at 58° , 15·8 parts; at 120° , 17 parts; and at 215° , 35·2 parts. It is insoluble in alcohol. It is decomposed with decrepitation by a red-heat, furnishing pure baryta: this decomposition should be effected in a porcelain crucible; for if platinum be used it is acted upon, and the baryta contaminated by oxide of platinum.

If a moderately-strong solution of nitrate of baryta be added to nitric

acid, a precipitation of nitrate of baryta takes place, in consequence of the difficult solubility of the nitrate in the dilute acid; in the concentrated acid the nitrate is quite insoluble: hence, in using nitrate of baryta as a test of the presence of sulphuric acid in nitric acid, the latter should be considerably diluted previous to its application, lest the precipitated nitrate of baryta be mistaken for sulphate. Nitrate of baryta is composed of

						Berzelius.	Kirwan.
Baryta	1	...	77	...	58·7	...	57
Nitric acid	1	...	54	...	41·3	...	43
<hr/>							
Nitrate of baryta	1		131		100·0		100

SULPHURET OF BARIUM. BaS , is formed, 1. By passing sulphuretted hydrogen over red-hot baryta in a coated glass or porcelain tube, as long as water is formed; it yields a grey granular compound. $\text{BaO} + \text{HS} = \text{BaS} + \text{HO}$. 2. By passing hydrogen over finely-powdered sulphate of baryta at a bright red-heat. $\text{BaO}, \text{SO}_3 + 4\text{H} = \text{BaS} + 4\text{HO}$. 3. By the action of charcoal upon ignited sulphate of baryta. $\text{BaO}, \text{SO}_3 + 4\text{C} = \text{BaS} + 4\text{CO}$. Mix sulphate of baryta, in fine powder, into a paste, with an equal volume of flour, place it in a Hessian crucible, on which a cover is luted, and expose it to a white-heat for an hour or two, raising the temperature slowly. On pouring hot water on the ignited mass the sulphuret of barium is dissolved, and may be separated from undecomposed sulphate and excess of charcoal by filtration. (TURNER.) It is readily soluble in hot water, and the solution, on cooling out of the contact of air, deposits hydrated crystals. By exposure to air, the solution absorbs carbonic acid and oxygen, yielding carbonate and hyposulphite of baryta. It dissolves sulphur, forming, according to Berzelius, a *pentasulphuret*. When its solution is boiled with oxide of copper till it ceases to blacken acetate of lead, and filtered whilst hot, it yields on evaporation pure baryta; mixed with carbonate of potassa it yields carbonate of baryta; with hydrochloric acid, chloride of barium; and with dilute nitric acid, nitrate of baryta. (See *Sulphate of Baryta*.) The difficulty with which sulphuret of barium is decomposed by the joint action of heat and air, is noticed by Berzelius, who observes, that in analysis, when sulphate of baryta contained in a filter is ignited, a portion of it is always reduced by the charcoal of the paper to the state of sulphuret, and that it always therefore gives off sulphuretted hydrogen by the action of hydrochloric acid. Sulphuret of barium consists of

Barium	1	...	69	...	81·2
Sulphur	1	...	16	...	18·8
<hr/>					
Sulphuret of barium	1		85		100·0

HYPOSULPHITE OF BARYTA. DITHIONITE OF BARYTA. $\text{BaO}, \text{S}_2\text{O}_2$. This salt is thrown down on pouring a solution of chloride of barium into a solution, not too dilute, of hyposulphite of lime: it is a white powder, soluble without decomposition in hydrochloric acid; at a low heat it takes fire, and sulphur burns off. When the solutions from which it is precipitated are dilute, it falls after some minutes, in small crystalline grains, followed by a copious separation of the salt. (HERSCHEL, *Edin. Phil. Journ.*, i. 20.) When a solution of sulphuret of barium is long

exposed to air, difficultly soluble acicular crystals of hyposulphite are deposited. This salt consists of

					II. Rose.
Baryta	1	...	77	...	57.46
Hyposulphurous acid	1	...	48	...	35.82
Water	1	...	9	...	6.72
				
Crystallized hyposulphite of baryta	1		134		100.00

SULPHITE OF BARYTA. BaO,SO_2 , is nearly insoluble in water; it is formed by adding sulphite of potassa to a solution of chloride of barium; or by passing sulphurous acid gas through water holding finely-divided carbonate of baryta in suspension. It dissolves sparingly in sulphurous acid, and the solution furnishes acicular and tetrahedral crystals when very slowly evaporated. It passes into sulphate by long exposure to air: at a red heat it gives out sulphur and becomes sulphate. It consists of

Baryta	1	...	77	...	70.6
Sulphurous acid	1	...	32	...	29.4
				
Sulphite of baryta	1		100		100.0

SULPHURETTED HYPOSULPHATE OF BARYTA. TRITHIONATE OF BARYTA. BaO,S_3O_5 . Sulphuretted hyposulphuric acid gives a white difficultly-soluble precipitate with baryta-water. (LANGLOIS.) The salt is also obtained by adding trithionate of potassa to chloride of barium?

BISULPHURETTED HYPOSULPHATE OF BARYTA. TETRATHIONATE OF BARYTA. BaO,S_4O_5 . Obtained by adding iodine to hyposulphite of baryta and water, till the mixture begins to acquire color. (See the corresponding soda salt: p. 614.) Iodide of barium and the above salt, both of which are soluble, are formed, but the bisulphuretted hyposulphate not having water enough to retain it in solution, gradually separates: alcohol is then added to remove the iodide of barium and excess of iodine, and the bisulphuretted salt remains as a white crystalline powder; it is best obtained in a crystallized state by adding alcohol to its concentrated aqueous solution, when its crystals are gradually deposited; it has a bitter taste, and acquires a yellow tint when exposed to humid air. It is not decomposed like the hyposulphites by hydrochloric acid; nitric acid rapidly acts upon it, evolving red fumes and throwing down sulphur. With chlorine it yields chloride of sulphur, which falls; but if the solution is much diluted chlorine converts the whole of the sulphur into sulphuric acid. The other bisulphuretted hyposulphates may be obtained by the addition of solutions of sulphates to this salt, in which case sulphate of baryta falls: the salts of potassa, soda, iron, zinc, and copper were thus obtained: they are almost all soluble, and slowly change in the air; at a higher temperature they are resolved into sulphur, sulphurous acid, and sulphates. Fordos and Gélis give the following composition of this salt (*Ann. Ch. et Ph.*, Decr., 1842, p. 492,) the crystals including 2 atoms of water.

					Fordos and Gélis.
Sulphur	4	...	64	...	32.2
Oxygen	5	...	40	...	20.1
Baryta	1	...	77	...	38.6
Water	2	...	18	...	9.1
				
Crystallized bisulphuretted hypo- sulphate of baryta }	1		199		100.0
					100.000

HYPOSULPHATE OF BARYTA. DITHIONATE OF BARYTA. $\text{BaO}, \text{S}_2\text{O}_5$. When sulphurous acid gas is passed into water holding finely-powdered peroxide of manganese in suspension, a neutral solution is obtained, composed of sulphate and hyposulphate of manganese. These salts are decomposed by excess of baryta, and a soluble *hyposulphate of baryta* is formed, through which carbonic acid is passed, in order to saturate any excess of baryta; and the whole being heated to drive off carbonic acid, which holds a little of the carbonate in solution, the hyposulphate of baryta is obtained, and may be purified by crystallization. (The solution of this salt may be decomposed by the careful addition of sulphuric acid, and the *hyposulphuric acid* is thus obtained in solution, as already stated, p. 402).

Hyposulphate of baryta crystallizes in quadrangular prisms, variously terminated. It dissolves, according to Gay Lussac, in 1.1 times its weight of water at 212° ; in 4 times its weight at 64° . It is insoluble in alcohol. At a red-heat it gives out water and sulphurous acid, and leaves seven-tenths of its weight of neutral sulphate of baryta. The crystallized salt consists of

					Welter and Gay Lussac.		Heeren.
Baryta	1	...	77	...	46.1	...	45.93
Hyposulphuric acid	1	...	72	...	43.1	...	43.31
Water.....	2	...	18	...	10.8	...	10.76
	<hr/>		<hr/>		<hr/>		<hr/>
	1		167		100.0		100.00

When a solution of this bihydrated salt is set aside to evaporate spontaneously, large four-sided prismatic crystals, terminated by four-sided pyramids, are gradually deposited, which, according to Heeren, are a *quaterhydrated hyposulphate of baryta*, composed therefore of

						Heeren.	
Baryta	1	...	77	...	41.6	...	41.88
Hyposulphuric acid.....	1	...	72	...	38.9	...	39.49
Water	4	...	36	...	19.5	...	18.63
	<hr/>		<hr/>		<hr/>		<hr/>
	1		185		100.0		100.00

SULPHATE OF BARYTA. BaO, SO_3 is an abundant natural product; it is insoluble in hot and cold water (according to some, soluble in from 40 to 50000 parts of water, but not more soluble in hot or in acidulated water, or in solutions of sal-ammoniac or common salt,) and therefore precipitates whenever sulphuric acid, or a soluble sulphate, is added to any soluble salt of baryta; hence the solutions of baryta are accurate tests of the presence of sulphuric acid, and are also used in analysis to determine its quantity. If sulphuric acid be poured upon caustic baryta, the heat is so intense as to cause ignition: but K hlman remarks that the acid containing exactly 1 atom of water (sp. gr. 1.845,) has no action on baryta at common temperatures, and that the violent action just noticed only ensues when the acid contains a little more or a little less water. If, however, baryta moistened with SO_3, HO , be touched with a hot iron, or with a glass rod dipped in water, the action immediately commences: so it does also if the baryta has been exposed to moist air. Baryta absorbs the vapor of anhydrous sulphuric acid with intense ignition. (*Ann. der Pharm.*, xxvii. 22.) If the hydrated acid be boiled upon the finely-powdered or

recently-precipitated sulphate, a portion is taken up; the whole of which, however, falls again upon diluting the solution with water. The extreme insolubility of this sulphate renders the soluble salts of baryta such delicate tests of the presence of sulphuric acid, that a millionth part in solution may, according to Pfaff, be detected by a slight white cloud. When the sulphuric acid is in combination the test is somewhat less delicate, but it shows the presence of 1 part of sulphate of soda in 400,000 of water. Recently-precipitated sulphate of baryta is sometimes very obstinate in subsiding from water, and will not only long remain suspended, but adheres to the glass, and will even pass through filtering-paper: heat, and a little excess of acid, generally facilitates its deposition. It may be safely heated to redness without risk of change, and hence the filter containing it, in some cases of quantitative analysis, may be conveniently burned away, except that the carbon of the paper converts a very minute portion of the sulphate into sulphuret.

Sulphate of baryta is an anhydrous compound of

						Klaproth.	Berzelius.		
Baryta.....	1	...	77	...	65·8	...	66·7	...	65·643
Sulphuric acid	1	...	40	...	34·2	...	33·3	...	34·357
<hr/>									
Sulphate of baryta	1		117		100·0		100·0		100·000

Native Sulphate of Baryta, Heavy Spar, or Baroselenite, is principally found in the mines of Westmoreland and Cumberland, and in Transylvania, Hungary, Saxony, and Hanover. A mammellated variety met with in Derbyshire, is called *cawk*. It occurs massive, stalactitic, and crystallized in a great variety of forms. Its primitive figure is a rhomboidal prism, the angles of which are $101^{\circ} 42'$, and $78^{\circ} 18'$. It is harder than carbonate of lime, but not so hard as fluor-spar. Its specific gravity is 4.7.

When native sulphate of baryta is heated it decrepitates, and at a very high temperature fuses into an opaque white enamel: it was employed in the manufacture of *jasper-ware* by the late Mr. Wedgwood, and for the production of opaque white patterns and figures upon a colored ground. When formed into a thin cake with paste, and heated to redness, (forming a mixture of sulphate of baryta, sulphuret of barium, and charcoal,) it acquires the property of phosphorescence, as was first ascertained by Vincenzo Cascariolo of Bologna, whence the term *Bologna phosphorus* (p. 118.) The artificial sulphate of baryta, which may be obtained in a very finely divided state, is used as a pigment, under the name of *permanent white*; it is useful for marking phials and jars in a laboratory, not being discolored by sulphuretted hydrogen, as is the case with white lead; but it does not form a body with linseed oil, and therefore when white lead is adulterated with sulphate of baryta, that property is proportionately deteriorated (see *white lead*.) Sulphate of baryta, in consequence of its cheapness and weight, is employed in various other cases of adulteration: it is the only baryta compound which is not poisonous. It combines by fusion with chloride of sodium and chloride of barium. (BERTHIER.)

Decomposition of Sulphate of Baryta. As the native sulphate is a common and abundant compound, several processes have been contrived for obtaining from it pure baryta. This may be effected by reducing the

crystallized sulphate to a fine powder, and heating it red-hot for half an hour in a silver crucible with three parts of carbonate of potassa: the fused mass is then boiled repeatedly in water, till it no longer affords anything soluble in that liquid; the insoluble residue, consisting chiefly of carbonate of baryta, may be digested in dilute nitric acid, by which nitrate of baryta is formed, and which will yield pure baryta by exposure to heat as above mentioned. Another method consists in exposing to a red-heat, in an earthen crucible, a mixture of 6 parts of finely-powdered sulphate of baryta with 1 of powdered charcoal, for half an hour. This converts the sulphate into sulphuret, which is to be dissolved in hot water, the solution filtered and mixed with solution of carbonate of soda as long as it occasions a precipitate, which, when washed and dried, is carbonate of baryta. Or, by adding hydrochloric acid to the liquid sulphuret, sulphur is thrown down, sulphuretted hydrogen evolved, and chloride of barium formed, which may be filtered off, and if required, decomposed by carbonate of potassa. Or the sulphuret, as it comes out of the crucible, may be thrown into *dilute* nitric acid, by which sulphuretted hydrogen is evolved, and nitrate of baryta formed, from the solution of which crystals are easily obtained by evaporation. Another method of decomposing a solution of sulphuret of barium consists in adding to it oxide of copper till it ceases to blacken acetate of lead; it may then be quickly filtered, and a solution of baryta is obtained. (MOHR.) In this process 6 equivalents of sulphuret of barium and 8 of oxide of copper produce 5 of baryta, 1 of hyposulphite of baryta, and 4 of subsulphuret of copper. $6\text{BaS} + 8\text{CuO} = 5\text{BaO} + \text{BaO}, \text{S}_2\text{O}_2 + 4\text{Cu}_2\text{S}$. Peroxide of manganese may be substituted for oxide of copper, but it generally gives a solution of baryta colored by some impurity; in this case the action is as follows: $6\text{BaS} + 4\text{MnO}_2 = 5\text{BaO} + \text{BaO}, \text{S}_2\text{O}_2 + 4\text{MnS}$. (GRAHAM.) When sulphate of baryta, in very fine powder, is boiled in a solution of carbonate of potassa or soda, a portion of the sulphate is also decomposed, and an equivalent proportion of carbonate of baryta formed: this decomposition of the sulphate is, however, never entire. (See p. 137.)

PHOSPHURET OF BARIUM is produced by passing phosphorus over heated baryta; there is an intense action, and phosphate of baryta, together with a phosphuret of a metallic lustre, is obtained, which acts upon water, evolving phosphuretted hydrogen, and affords a solution containing hypophosphite of baryta. (It is probable that the mutual action of phosphorus and baryta at high temperatures is analogous to that of phosphorus and lime. See *phosphuret of lime*, p. 649.)

HYPOPHOSPHITE OF BARYTA. BaO, PO , may be obtained by boiling phosphorus with baryta in water, or by the action of phosphuret of baryta on water; like the other hypophosphites, it is very soluble in water, and difficultly crystallizable. (DULONG, *Ann. Ch. et Ph.*, ii. 142.) It forms, according to H. Rose, two hydrates, with 2 and 3 atoms of water. (*Poggend.*, ix. and xii. See also WURTZ. *Ann. der Pharm.*, xliii.)

PHOSPHITE OF BARYTA. BaO, PO_3 , was obtained by Berzelius, by adding a solution of chloride of barium to phosphite of ammonia; a

crystalline crust of phosphite of baryta was formed in 24 hours. (*Ann. Ch. et Ph.*, ii. 231.) A red-heat converts it into pyrophosphate of baryta with the evolution of hydrogen. It consists of

						Berzelius.
Baryta	2	...	154	...	67.5	67.24
Phosphorous acid	1	...	56	...	24.5	24.31
Water	2	...	18	...	8.0	8.45
<hr/>						<hr/>
Crystallized phosphite of baryta	1		228		100.0	100.00

When this phosphite is dissolved in phosphorous acid, it yields by evaporation over sulphuric acid in vacuo granular crystals of a salt= $2\text{BaO}, 2\text{PO}_3, 5\text{HO}$, or perhaps $2 [\text{BaO}, 2\text{HO}, \text{PO}_3] + \text{HO}$. (H. ROSE. *Poggend.*, ix. 215.) The formula of the neutral salt adopted by Wurtz is $2\text{BaO}, \text{PHO}_4, \text{HO}$, and he represents the *acid phosphite* by $\text{BaO}, \text{PHO}_4, \text{HO} + \text{HO}$. (*Ann. Ch. et Ph.*, Fevr., 1846.)

PHOSPHATES OF BARYTA. 1. *Tribasic Phosphates.*

a. Subphosphate. $3\text{BaO}, c\text{PO}_5$, is thrown down from a solution of chloride of barium by tribasic phosphate of soda, the liquid remaining neutral. (GRAHAM.) It consists of

Baryta	3	...	231	...	76.24
Phosphoric acid	1	...	72	...	23.76
<hr/>					
Subphosphate of baryta	1		303		100.00

β. Common Phosphate. $2\text{BaO}, \text{HO}, c\text{PO}_5$. This salt (corresponding to the common phosphate of soda) is formed by dropping solution of common phosphate of ammonia into chloride of barium so as to leave the latter in excess; it is a white pulverulent precipitate, easily soluble in dilute hydrochloric, nitric, and phosphoric acids, and in solutions of hydrochlorate, nitrate, and succinate of ammonia, but almost insoluble in water. Its constituents are

Baryta	2	...	154	...	65.53
Water	1	...	9	...	3.84
Phosphoric acid	1	...	72	...	30.63
<hr/>					
Common phosphate of baryta	1		235		100.00

γ. Phosphate of Baryta and Water. Biphosphate of Baryta. $\text{BaO}, 2\text{HO}, c\text{PO}_5$. This salt corresponds to the so-called biphosphate of soda. It is formed by adding phosphoric acid to the common phosphate and slowly evaporating the liquor: its crystals are resolved, by a large excess of water, into free phosphoric acid and common phosphate. (BERZELIUS.) The crystals contain

						Berzelius.
Baryta	1	...	77	...	46.10	46.46
Water	2	...	18	...	10.77	11.00
Phosphoric acid	1	...	72	...	43.13	42.54
<hr/>						<hr/>
Biphosphate of Baryta	1		167		100.00	100.00

2. *Bibasic Phosphate. Pyrophosphate of Baryta.* $2\text{BaO}, b\text{PO}_5$. When anhydrous pyrophosphate of soda ($2\text{NaO}, b\text{PO}_5$) obtained by heating the common phosphate, is dissolved in water, and added to chloride of barium, a precipitate of pyrophosphate falls; it is soluble in a solution

of sal-ammoniac. (GMELIN.) The same bibasic salt would be obtained by heating β to redness: it contains

Baryta	2	154	68.14	Hess. 67.33
Phosphoric acid	1	72	31.86	32.67
<hr/>							
Pyrophosphate of baryta	1		226		100.00		100.00

3. *Monobasic Phosphate. Metaphosphate of Baryta.* $\text{BaO}, \alpha\text{PO}_5$. When excess of chloride of barium is added to a solution of metaphosphate of soda in a small quantity of water, a gelatinous precipitate falls, which when washed and dried, becomes a translucent brittle mass insoluble in hot water, but which, when long boiled in water, gradually yields a solution of the tribasic phosphate of baryta and water above described (γ), and then precipitates silver yellow. This salt contains, after it has been ignited,

Baryta	1	77	51.67	Graham. 52.04
Phosphoric acid	1	72	48.33	47.96
<hr/>							
Metaphosphate of baryta	1		149		100.00		100.00

SELENIURET OF BARIUM. BaSe , is the result of passing hydrogen gas over seleniate of baryta at a red-heat: it is soluble in water. (BERZELIUS.)

SELENITE OF BARYTA. BaO, SeO_2 falls in the form of a white insoluble powder, when solution of selenite of potassa is added to chloride of barium. *Biselenite of baryta* is formed by dissolving carbonate of baryta in selenious acid; it forms a granular crystalline powder very difficultly soluble in water.

SELENIATE OF BARYTA. BaO, SeO_3 , resembles the sulphate in insolubility.

CARBONATE OF BARYTA. BaO, CO_2 . This salt falls in the form of a white powder, when the soluble salts of baryta are precipitated by the alkaline carbonates. For this purpose carbonate of ammonia is preferable to the carbonate of soda or potassa, for portions of the fixed alkalis are apt to go down with the baryta, and carbonate of potassa is seldom quite free from silica and sulphates. Other methods of obtaining carbonate of baryta are stated under the head *Sulphate of Baryta*. It is so nearly insoluble, that water at 60° only takes up about 1-4300th, and at 212° about 1-2300th part. Water saturated with carbonic acid dissolves 1-820th. It has a very slight alkaline action on vegetable colors: it is highly poisonous. When *baryta-water* is added to solutions of the carbonated alkalis, it abstracts their carbonic acid; when agitated with a cold solution of sulphate of potassa or soda, finely divided carbonate of baryta gradually forms sulphate of baryta, and carbonated alkali is retained in solution; but the inverse changes ensue on boiling. Freshly precipitated carbonate of baryta is soluble in solutions of hydrochlorate, nitrate, and succinate of ammonia, and by boiling, carbonate of ammonia is in these cases evolved. It is insoluble in solutions of potassa and soda salts; but when a very dilute barytic solution is added to bicar-

bonate of potassa or soda a small portion of carbonate of baryta is retained in solution.

When a solution of chloride of barium is decomposed by sesquicarbonate of potassa, a sesquicarbonate of baryta falls $=2\text{BaO}, 3\text{CO}_2$: it is somewhat more soluble in water than the carbonate. (BOUSSINGAULT. *Ann. Ch. et Ph.*, xxviii. 288.) Carbonate of baryta consists of

						Withering.	Berzelius.
Baryta.....	1	...	77	...	77.78	...	77.9
Carbonic acid	1	...	22	...	22.22	...	22.1
<hr/>							
Carbonate of baryta	1		99		100.00		100.0

Native Carbonate of Baryta was first discovered at Anglesark, in Lancashire, by Dr. Withering, and hence acquired the name of *Witherite*. It has also been found in Wales, Cumberland, Durham, Westmoreland, and Shropshire. Its primitive crystal is an obtuse rhomboid: sometimes it forms pyramidal six-sided prisms. That found in Lancashire is in globular masses of a radiated structure. Its density is 4.33. It is useful as a source of pure baryta and its salts. Though scarcely soluble in water, it is poisonous, probably in consequence of its solubility in the acids of the stomach. It dissolves more sparingly in solution of carbonic acid than the precipitated carbonate, and is more difficultly decomposed; but if mixed with charcoal-powder, and kept for some time at a high red-heat, carbonic oxide escapes, and pure baryta is formed.

A *double carbonate of lime and baryta*, under the name of *Baryto-calcite*, from Alston Moor, has been described by Brooke and Children (*Ann. Phil.*, 2 Ser., III. 76) $=\text{CaO}, \text{BaO}, 2\text{CO}_2$. Thomson has mentioned another variety $=2[\text{CaO}, \text{CO}_2], + \text{BaO}, \text{CO}_2$. (*Mineralogy*, I. 142.) The forms and composition of these minerals have been investigated by Descloizeaux and Delesse. (*Ann. Ch. et Ph.*, Avril, 1845.)

CYANIDE OF BARIUM, BaCy , is precipitated in the form of a white powder when hydrocyanic acid is mixed with baryta-water. It is also formed by heating ferrocyanide of barium in a retort, for it is not decomposed at a temperature which destroys the cyanide of iron. It is sparingly soluble in water, and the solution soon becomes covered by a film of carbonate of baryta, when in contact with air.

CYANATE OF BARYTA, BaO, CyO . When cyanogen is passed through a mixture of hydrate of baryta and water, cyanate of baryta and cyanide of barium are formed: the latter may be decomposed by a stream of carbonic acid: the filtered liquor then yields, when concentrated by evaporation and mixed with alcohol, small prismatic crystals; when their aqueous solution is evaporated, it decomposes into carbonate of baryta and ammonia.

MELLONIDE OF BARIUM, BaMe , is obtained in the form of a yellow precipitate when solutions of mellonide of potassium and chloride of barium are mixed; it dissolves in boiling water, and the solution deposits acicular crystals on cooling which contain 6 atoms of water, 5 of which are evolved at 265° . (LIEBIG.)

SULPHOCYANIDE OF BARIUM, BaO, Csy , is formed by heating ferrocyanide of barium with sulphur: it is soluble in water, and forms brilliant acicular crystals, which are slightly deliquescent: they contain 2 atoms of water. When fused this salt concretes into a brown crystalline mass on cooling.

BORATE OF BARYTA, $\text{BaO}, 2\text{BO}_3$, is formed by mixing a soluble salt of baryta with a solution of borax, and fusing the washed precipitate: it is a grey transparent glass, very sparingly soluble in water; before fusion it is a *hydrated salt* $= \text{BaO}, 2\text{BO}_3, 2\text{HO}$, somewhat more soluble in water, and its solution is decomposed by carbonic acid. (BERZELIUS.) It is composed of

				Thenard.	Berzelius.	L. Gmelin.	Tünnermann.
Baryta	1	77	52.38	57.8	55.8	54.9	52.79
Boracic acid	2	70	47.62	42.2	44.2	45.1	47.21
<hr/>							
Borate of baryta....	1	147	100.00	100.0	100.0	100.0	100.00

BOROFLUORIDE OF BARIUM. $\text{BaF}, \text{BF}_3, 2\text{HO}$. Carbonate of baryta is added to the aqueous solution of fluoboric acid, as long as it is dissolved: on evaporation some boracic acid first separates, and afterwards prismatic crystals of the borofluoride, soluble in water without decomposition, and deliquescent in damp air: they contain 10.34 *per cent.* of water: they are decomposed at a red-heat; liquid fluoboric acid first passes off, then fluoboric gas; and fluoride of barium remains: (BERZELIUS:) they consist of

					Berzelius.
Fluoride of barium	1	88	50.57	}	89.51
Fluoboric acid	1	68	39.08		
Water	2	18	10.35		
<hr/>					
Crystallized borofluoride of barium	1	174	100.00		100.0

PROPERTIES OF BARYTIC SALTS. The soluble barytic salts furnish white precipitates of carbonate and sulphate of baryta, upon the addition of carbonate or sulphate of soda. They give a greenish yellow tinge to the flame of spirit of wine. The sulphate is insoluble in nitric acid and in the alkalis, and very sparingly soluble in sulphuric acid. All the other barytic salts are soluble in dilute hydrochloric or nitric acid, and their solutions give a white precipitate with solutions of sulphuric acid and the sulphates. A saturated aqueous solution of sulphate of strontia is a test for the salts of baryta; it requires to be used in pretty large quantity, and the solutions to be tested should be nearly neutral. Nearly all the barytic compounds are poisonous: sulphate of baryta is, however, harmless: the safest antidote, therefore, for the soluble barytic salts, is solution of sulphate of soda, and in poisoning by the carbonate it has been proposed to use a mixture of vinegar with an alkaline sulphate, an emetic or the stomach-pump having been previously resorted to. Chloride of barium has been employed in medicine, but the principal use of baryta is in the chemical laboratory, where baryta-water is kept as a test of the presence of carbonic acid, and the nitrate, chloride, and acetate of barium are employed in the quantitative and qualitative determination of sulphur, sulphuric acid, and the sulphates.

§ VI. STRONTIUM. Sr. 44.

Strontia (or *strontites*) was first discovered in the state of *carbonate* at Strontian in Argyleshire, and was supposed to be a carbonate of baryta. Crawford, in 1790, pointed out some of its distinctive characters, but it was first shown to contain a peculiar earth by Dr. Hope, in 1792, (*Edin. Phil. Trans.*, iv.,) and by Klaproth in 1793, (*Crell's Annals*, 1793 and 1794.) It is a substance of rare occurrence. The existence of *strontium*, as the metallic base of the earth *strontia*, was first demonstrated by Davy in 1808. It is probably as heavy as barium, and resembles it in appearance and in its leading chemical characters; it has, however, been as yet very imperfectly examined. The equivalent of strontium deduced from the best analyses of its compounds is 44, (43·8 TURNER, 43·85 GRAHAM, 44 GMELIN.)

PROTOXIDE OF STRONTIUM. STRONTIA. SrO . Strontium is rapidly oxidized by exposure to air, and it decomposes water at common temperatures, evolving hydrogen, and forming the oxide. Strontia may be obtained from the nitrate, the carbonate, and the sulphate of strontia, by processes similar to those directed in regard to baryta. It is a greyish-white porous substance: its specific gravity is 3·9; it is extremely infusible, not volatile, has an acrid taste, and an alkaline reaction upon vegetable colors. It consists of

						Stromeyer.	Davy.	Berzelius.
Strontium	1	44	84·6 84·67 86 84·55
Oxygen	1	8	15·4 15·33 14 15·45
<hr/>						<hr/>	<hr/>	<hr/>
Strontia	1		52		100·0	100·00	100	100·00

HYDRATE OF STRONTIA. SrO, HO . When strontia is sprinkled with water it heats and falls to powder like baryta, forming a white solid hydrated compound of 1 equivalent of strontia = 52, and 1 of water = 9; it fuses, but does not part with its water, at a red heat, but when subjected for a long time to a higher temperature, it gradually becomes anhydrous. It is insoluble in alcohol. It dissolves in about 160 parts of water at 60°, forming *strontia-water*. Boiling water dissolves it more abundantly, and on cooling deposits crystals in the form of thin quadrangular tables: their primary form is a right square prism (BROOKE, *Ann. of Phil.*, 2nd Series, vii. 287): they are soluble in 50 parts of cold and 2 of boiling water (DALTON), and are converted by heat into the protohydrate. They contain according to Phillips (*Phil. Mag.*, 3rd Series, vi. 52) 63·76 *per cent.* of water, and consist, therefore, of 1 equivalent of strontia = 52, and 10 equivalents of water = 90: or, according to Denham Smith (*Phil. Mag.*, ix. 87), 9 equivalent of water, being between 60 and 61 *per cent.*

PEROXIDE OF STRONTIUM has not been formed by passing oxygen over heated strontia. When peroxide of hydrogen is mixed with strontia-water, brilliant crystalline scales are thrown down, composed according to Thenard of 1 equivalent of strontium and 2 of oxygen. SrO_2 . Dumas says that strontia does not absorb oxygen when it is heated in that gas, but that the precipitate thrown down by oxygenated water is a hydrated binoxide of strontium.

CHLORIDE OF STRONTIUM. SrCl . When strontia is heated in chlorine, it evolves 1 volume of oxygen for every 2 volumes of chlorine that are absorbed, and a chloride of strontium is the result. Heated in hydrochloric acid, strontia absorbs the gas with ignition and evolution of water. Chloride of strontium is generally obtained by dissolving *carbonate of strontia* in diluted hydrochloric acid, evaporating to dryness, and fusing the residue. It is of a grey color and an acid taste; its sp. gr. 2·8. It dissolves in alcohol, and the solution burns with a purplish-red flame. Its aqueous solution furnishes, upon evaporation, hexagonal prismatic crystals, which are deliquescent and soluble in 0·75 parts of water at 60° . They contain 40·5 *per cent.* of water of crystallization (BERZELIUS): hydrochloric acid added to the concentrated solution throws down part of the salt. The crystals are soluble in 24 parts of cold, and 19 of boiling absolute alcohol, but much more soluble in ordinary alcohol. 100 parts of anhydrous chloride of strontium rapidly absorb 84·5 of dry ammonia, falling into a light bulky powder, which loses ammonia when heated. (H. ROSE, *Ann. Ch. et Ph.*, LXii. 316.) The anhydrous or fused chloride consists of

						Davy.
Strontium	1	44	55 58
Chlorine	1	36	45 42
<hr/>						
Chloride of strontium	1		80		100	100

The crystals contain

The crystals contain					Vauquelin.
Strontium	1	44 32·83	} 60
Chlorine	1	36 26·86	
Water	6	54 40·31	
<hr/>					<hr/>
Hydrated chloride of strontium.....	1		134	100·00	100

CHLORATE OF STRONTIA, SrO, ClO_5 , is obtained in the same way as the chlorate of baryta; it is a very soluble and deliquescent salt, difficultly crystallizable, and detonates when thrown upon red-hot coals with a beautiful purple light. Very soluble in alcohol (CHENEVIX); insoluble (WÄCHTER.)

PERCHLORATE OF STRONTIA, SrO, ClO_7 , is a very deliquescent salt: its alcoholic solution burns with a beautiful purple flame. (SERULLAS, *Ann. Ch. et Ph.*, XLvi. 304.)

IODIDE OF STRONTIUM, SrI , may be formed as iodide of barium. Dissolved in water, and carefully evaporated, it furnishes delicate prismatic crystals (*Hydriodate of Strontia*), which heated in close vessels, fuse without decomposition; heated in the open air, iodine escapes, and strontia is generated. Iodide of strontium consists of

Strontium	1	44	26
Iodine	1	126	74
<hr/>					
Iodide of strontium	1		170		100

IODATE OF STRONTIA, SrO, IO_5 , is obtained as iodate of baryta: when iodine is added to strontia water, the iodate falls and iodide remains in solution. When solution of chloride of strontium is decomposed by iodate of soda, the precipitated iodate of strontia differs in its state of

hydration with the temperature: if the liquid is *hot* a white pulverulent *monohydrate* falls = $\text{SrO},\text{IO}_5,\text{HO}$: if *cold*, small octohedral crystals of *hexhydrated iodate* are formed = $\text{SrO},\text{IO}_5,6\text{HO}$: they are difficultly soluble, requiring about 400 parts of cold and 120 to 130 of boiling water. (RAMMELSBERG, *Poggend.*, XLIV. 575.)

PERIODATE OF STRONTIA. The salt which remains after heating the iodate to redness is a subperiodate = $5\text{SrO},\text{IO}_7$. (RAMMELSBERG.)

BROMIDE OF STRONTIUM, SrBr . Carbonate of strontia dissolved in hydrobromic acid and evaporated to dryness leaves a white fusible bromide: it crystallizes from its aqueous solution in long slender prisms = $\text{SrBr},6\text{HO}$. (BERTHEMOT, *Ann. Ch. et Ph.*, LXXIV. 394. RAMMELSBERG, *Poggend.*, LV. 238.) Bromide of strontium absorbs ammonia, forming a compound = $4\text{SrBr} + \text{NH}_3$.

BROMATE OF STRONTIA. SrO,BrO_5 . By evaporating solution of carbonate of strontia in bromic acid, crystals are obtained = $\text{SrO},\text{BrO}_5,\text{HO}$: they are rhombic prisms, soluble in 3 of cold water, which become anhydrous after exposure to a heat of 248° . (RAMMELSBERG.)

FLUORIDE OF STRONTIUM, SrF , is a very difficultly soluble white powder, obtained in the same way as fluoride of barium.

NITRATE OF STRONTIA. SrO,NO_5 . This salt is obtained by processes similar to those for obtaining *nitrate of baryta*: it crystallizes in octohedrons: it is soluble in 5 parts of water at 60° , and in half its weight of boiling water. It is insoluble in anhydrous alcohol. Its taste is pungent and cooling. At a red-heat the acid is evolved and decomposed, and strontia remains. According to Stromeyer, the crystallized salt, as ordinarily prepared, contains no water of crystallization. It is used in the *red fire* employed at the theatres, which consists of 40 parts of dry nitrate of strontia, 13 of powdered sulphur, 5 of chlorate of potassa, and 4 of sulphuret of antimony. The chlorate and sulphuret should be separately powdered, and mixed together on paper with the other ingredients; a small quantity of powdered charcoal is also occasionally added. When nitrate of strontia is finely powdered and mixed with spirit of wine, it communicates a beautiful red tint to its flame. It is composed of

						Stromeyer.		Cooper.		Richter.	
Strontia	1	52	49	49.38	49.08	48.6
Nitric acid	1	54	51	50.62	50.92	51.4
<hr/>											
Nitrate of strontia	1		106		100		100.00		100.00		100.0

Hydrated nitrate of Strontia. $\text{SrO},\text{NO}_5,5\text{HO}$. When a moderately-strong solution of the above *anhydrous nitrate* is set aside, it sometimes deposits at a low temperature *oblique rhombic crystals*, (BROOKE, *Ann. of Phil.*, 2nd Series, vii. 288,) composed of

							Cooper.		Kirwan.
Strontia.....	1	52	34.44	35.4	36.21
Nitric acid	1	54	35.76	36.8	31.07
Water	5	45	29.80	27.8	32.72
<hr/>									
Hydrated nitrate of strontia	1		151		100.00		100.0		100.00

SULPHURET OF STRONTIUM, SrS , may be formed by exposing the powdered sulphate to a high red-heat with charcoal, and by other methods similar to those described under sulphuret of barium and sulphate of baryta (pp. 665 and 668.) It dissolves in water with the same phenomena as sulphuret of barium, and its solution furnishes, by cautious evaporation, crystals of *bihydrosulphuret of strontia* $= \text{SrS}, \text{HS}, \text{HO}$, together with hydrated strontia. When strontia or sulphuret of strontium is dissolved in water by a current of sulphuretted hydrogen, and the solution evaporated in vacuo, square prismatic crystals are obtained, which, when heated, fuse and give off water and sulphuretted hydrogen, sulphuret of strontium remaining in the form of a white powder. (BERZELIUS.)

HYPOSULPHITE (DITHIONITE) OF STRONTIA, $\text{SrO}, \text{S}_2\text{O}_2$, is formed by passing sulphurous acid into the solution of the sulphuret, or by exposing it to air: it crystallizes in rhomboids permanent at common temperatures, and soluble in about 5 parts of water at 60° . (GAY LUSSAC, *Ann. de Chim.*, LXXXV.) According to Herschel, this salt is doubly refractive. Its taste is bitter, and it is insoluble in alcohol. The crystals consist of

					Gay Lussac.
Strontia	1	52	35.9
Hypsulphurous acid	1	48	33.1
Water	5	45	31.0
<hr/>					<hr/>
Crystallized hypsulphite of strontia....	1		145		100.0

SULPHITE OF STRONTIA, SrO, SO_2 , is tasteless, nearly insoluble and becomes *sulphate* by exposure to air.

HYPOSULPHATE (DITHIONATE) OF STRONTIA, $\text{SrO}, \text{S}_2\text{O}_5$, crystallizes in hexangular tables, soluble in 4.5 water at 60° , and in 1.5 at 212° ; insoluble in alcohol; bitter, permanent, and leaving 0.577 of *sulphate* of strontia after heating to redness. They consist of

					Heeren.
Strontia	1	52	32.5
Hypsulphuric acid	1	72	45.0
Water.....	4	36	22.5
<hr/>					<hr/>
Crystallized hypsulphate of strontia	1		160		100.0

SULPHATE OF STRONTIA. SrO, SO_3 . It is of very sparing solubility, 1 part requiring 3840 of boiling water for its solution. (HOPE.) According to Andrews (*Phil. Mag.*, vii. 406), it dissolves in 3600 of water at 60° , but is less soluble when sulphuric acid or sulphate of soda are at the same time present. It is distinguished from sulphate of baryta by being slowly soluble in solution of chloride of sodium. (WACKENRODER.) It is insoluble in solution of sal-ammoniac. It is soluble in boiling sulphuric acid, but falls upon dilution. When heated with charcoal, its acid is decomposed, and *sulphuret of strontium* formed, which affords nitrate by the action of nitric acid. This process, as practised upon sulphate of baryta, is adopted to obtain the salts of strontia, and through them pure strontia. At a very high heat it fuses into an opaque enamel. According to Moretti, its acid is expelled at a red-heat, by arsenic acid. It consists of

					Vauquelin. Stromeyer. Klaproth.						
Strontia.....	1	...	52	...	56.52	...	54	...	57	...	58
Sulphuric acid	1	...	40	...	43.48	...	46	...	43	...	42
<hr/>					<hr/>					<hr/>	
Sulphate of strontia	1		92		100.00		100		100		100

Native Sulphate of Strontia is sometimes of a blue tint, and has hence been called *cælestine*. Sometimes it is colorless and transparent. Its primitive form is a prism of $104^{\circ} 48'$ and $75^{\circ} 42'$ with a rhomboidal basis. It has been found at Strontian, in Argyleshire; in the vicinity of Bristol; at Montmartre, near Paris; in Germany, America, &c. The finest crystallized specimens are accompanied with native sulphur, from Sicily. Its specific gravity varies between 3 and 4. A *baryto-sulphate of strontia*, composed of about 3 atoms of sulphate of baryta and 7 of sulphate of strontia, is found in Upper Canada; and another variety, called *radiated cælestine*, occurs at Nörden, near Hanover.

PHOSPHURET OF STRONTIUM, SrP , has properties analogous to those of phosphuret of barium.

HYPOPHOSPHITE OF STRONTIA, SrO, PO , has been examined by Dulong; it is a very soluble and difficultly-crystallizable salt, and is obtained by a process similar to that for forming the hypophosphite of baryta. (*Ann. Ch. et Ph.*, ii. 142.) Wurtz obtained it by boiling a solution of sulphuret of strontium with phosphorus: it is unchanged by air, very soluble in water, and insoluble in alcohol: its formula is $\text{SrO}, \text{PO}, 2\text{HO}$; or $\text{SrO}, \text{PH}_2, \text{O}_3$. (*Ann. Ch. et Ph.*, Fevr. 1846.)

PHOSPHITE OF STRONTIA. SrO, PO_3 . When carbonate of strontia is dissolved in phosphorous acid, a crystallized salt is obtained on evaporation; the crystals are decomposed by warm water, and a white powder falls, which is probably a neutral phosphite. (BERZELIUS.) When solution of chloride of strontium and chloride of phosphorus are mixed and exposed to spontaneous evaporation, crystals of phosphite of strontia are deposited; when they are heated, phosphuretted hydrogen is evolved, and phosphate of strontia formed.

PHOSPHATE OF STRONTIA (*Tribasic*), $2\text{SrO}, \text{HO}, \text{cPO}_5$, is an insoluble white salt; it is soluble in excess of phosphoric acid, and in dilute hydrochloric and nitric acids. It is entirely decomposed by sulphuric acid. By igniting it with charcoal, *phosphuret of strontium* is obtained. It fuses, before the blow-pipe, into a white enamel. It is obtained by precipitation from nitrate of strontia, by rhombic phosphate of soda, and consists of

Strontia	2	...	104	...	56.21
Water	1	...	9	...	4.86
Phosphoric acid	1	...	72	...	38.93
<hr/>					<hr/>
Common phosphate of strontia	1		185		100.00

Bibasic Pyrophosphate. $2\text{SrO}, \text{bPO}_5$. This salt is formed by heating the preceding to redness: it consists of

						Vauquelin.	
Strontia	2	...	104	...	59.69	...	58.76
Phosphoric acid	1	...	72	...	40.31	...	41.24
<hr/>			<hr/>		<hr/>		<hr/>
Bibasic or pyrophosphate of strontia,...	1		176		100.00		100.00

SELENITE OF STRONTIA is an insoluble white powder. (BERZELIUS, *Ann. Ch. et Ph.*, ix. 263.) There is also a difficultly soluble *biselenite*.

SELENIATE OF STRONTIA has not been examined.

CARBONATE OF STRONTIA, SrO, CO_2 , when artificially formed, is a white powder, soluble in 1536 parts of hot water. When strongly heated with a little charcoal-powder, it is decomposed, carbonic oxide is given off, and pure strontia remains (but it is not decomposed by heat alone?). When steam is passed over it at a high temperature, it parts with its acid and become a hydrate. Before the oxyhydrogen blow-pipe it slowly volatilizes with a red light. It is very slightly soluble by excess of carbonic acid, and the solution deposits small acicular crystals. It is composed of

						Stromeyer.	Ure.	Klaproth.			
Strontia	1	...	52	...	70.3	...	70.313	...	69.8	...	69.5
Carbonic acid.....	1	...	22	...	29.7	...	29.687	...	30.2	...	30.5
<hr/>											
Carbonate of strontia	...	1	74		100.0		100.000		100 0		100.0

Native Carbonate of Strontia or *Strontianite* is a rare mineral. It has a greenish tint, and occurs in radiated masses, and sometimes in acicular and hexahedral crystals. It was first discovered, in 1787, at Strontian, in Argyleshire, whence the name of this earth; it has also been found in Saxony, and in Peru. Its specific gravity is 3.6. It generally contains traces of carbonate of lime. When in very fine powder, it has a slight alkaline reaction upon vegetable colors.

CYANIDE OF STRONTIUM has not been examined.

MELLONIDE OF STRONTIUM is more soluble than the corresponding barytic salt: its hot saturated solution deposits abundance of acicular crystals on cooling.

SULPHOCYANIDE OF STRONTIUM forms delicate prismatic crystals, which deliquesce on exposure, and contain 3 atoms of water, which they do not lose till heated to between 320° and 340° , when they begin to decompose.

BORATE OF STRONTIA, $\text{SrO}, 2\text{BO}_3$, was formed by Dr. Hope. It is a white powder, soluble in 130 parts of water, and very soluble in solutions of nitrate and hydrochlorate of ammonia.

PROPERTIES OF THE SALTS OF STRONTIA. There is in many respects a resemblance between strontia and baryta, which has led to difficulties in analysis. They are both found native in the states of sulphate and carbonate only; both sulphates are slightly soluble in excess of sulphuric acid, nearly insoluble in water, and decomposable by similar means, as well as the native carbonates; they are both crystallizable from their hot aqueous solutions, and both attract carbonic acid. The carbonates are each soluble with effervescence in the stronger acids; but the native carbonates are not so easily acted on as the artificial. Pure ammonia precipitates neither one nor the other. The following are essential distinctions. Baryta and all its salts, except the sulphate, are poisonous. The corresponding strontitic salts are not so. Baryta tinges flame yellow; strontia, red; and this color is very brilliant with the flame of hot alcohol, and especially so with pyroligneous spirit. Strontia has less attraction for

acids than baryta; hence the strontitic salts are decomposed by baryta. Chloride of barium is insoluble in anhydrous alcohol, but chloride of strontium dissolves in about 24 parts of alcohol. The greater number of the barytic salts are less soluble than those of strontia; this even applies to the sulphates, for the sulphate of strontia is sensibly soluble in water, which the sulphate of baryta is not; hence the use above alluded to of an aqueous solution of sulphate of strontia as a test for barytic salts. The two classes of salts also differ in their respective forms. Pure baryta, moreover, is much more soluble in water than pure strontia. Baryta and strontia may also be distinguished by the following process: Dissolve in hydrochloric, nitric, or any other acid with which it forms a soluble salt, then add excess of solution of sulphate of soda, filter, and test the clear fluid by carbonate of potassa; if any precipitate falls, the earth was strontia; if none, baryta. This again shows the slight solubility of sulphate of strontia, and the insolubility (in such solution) of sulphate of baryta. Succinate of ammonia, and fluosilicic acid, precipitate baryta, but not strontia. Isomorphism pervades the salts of strontium, barium, and lead, and they are to a certain extent analogous in their respective solubilities.

§ VII. MAGNESIUM. Mg. 12.

MAGNESIUM, or, as he at first called it, *Magnium*, was discovered by Sir H. Davy in 1808: he obtained it by electrizing mercury in contact with magnesia, and also by passing the vapor of potassium over white-hot magnesia, and he observed its inaction upon water as compared with potassium.

The metallic base of magnesia had not, however, been accurately examined, till Bussy, in 1830, obtained it by the decomposition of *chloride of magnesium* by potassium. (*Ann. Ch. et Ph.*, XLVI.) To effect this, some globules of potassium are put into a glass tube, and fragments of anhydrous chloride of magnesium placed over them: the latter is then heated till it begins to fuse, and the potassium allowed to run through it by slightly inclining the tube; ignition ensues, and the mass, when cold, affords, on washing with water, a number of small metallic globules. Sodium placed at the bottom of a green glass test-tube, and covered with fragments of fused chloride of magnesium, when carefully heated from above downwards, also decomposes the chloride: in all these cases, the action is very intense, so that the tube is often broken and its contents lost. Becquerel, by the electrolysis of a solution of chloride of magnesium, obtained the metal in small octohedral crystals. Magnesium has much of the appearance of silver; though hard, it is malleable, and bears some resemblance to zinc. It fuses at a red-heat; and the small particles in which it is produced by the reduction of the chloride may be fused together at a bright red-heat under fused chloride of potassium.

Magnesium is not immediately acted upon by cold water, but it is rapidly dissolved by very dilute acids, forming solutions of magnesia. When heated in the flame of a spirit-lamp, it burns when in small particles with intense light into magnesia: it resists the action of dry air at common temperatures, but in damp air becomes gradually covered by a film of oxide. The equivalent of magnesium is 12. (12 GMELIN. 12·7 TURNER.)

OXIDE OF MAGNESIUM. MAGNESIA. MgO . This is the only known compound of magnesium and oxygen; it is generally procured by exposing the carbonate of magnesia for some time to a red-heat. Magnesia is a bulky white insipid powder, sp. gr. about 3: it has a slight alkaline reaction upon delicate vegetable colors, but water which has been agitated with magnesia, when filtered through paper, does not produce similar effects (HENRY); it is almost infusible, and a mixture of lime and magnesia is scarcely more fusible than the separate earths. It is nearly insoluble in water. Cold water is said to dissolve it in the proportion of between a six and seven thousandth part; whereas 1 part of the earth, according to Dr. Fyfe, requires for its solution 36,000 of boiling water. It does not absorb carbonic acid or moisture when exposed to air nearly so rapidly as the other alkaline earths, and scarcely any heat is produced by pouring water upon it, but it is converted into a *hydrate*. (MgO, HO .) When thrown down from its solutions by potassa, collected upon a filter, and dried at 212° , it still retains water; but when more highly heated, and at a temperature below redness, it again becomes anhydrous. It is insoluble in solutions of potassa and soda. It forms bitter saline compounds with the acids, and is most readily distinguished from the other earths by the solubility and bitter taste of its *sulphate*; the sulphates of the other alkaline earths being nearly or quite tasteless, or very difficultly soluble, while those of the earths proper are sweet or astringent. The attractions of magnesia for the acids correspond, in most instances, closely with those of ammonia, which is in some cases displaced by, and in others displaces, magnesia. It may also be observed, that ammonia and magnesia produce double salts with most of the acids. Magnesia consists of

						Wollaston.	Gay Lussac.	Berzelius.
Magnesium	1	12	60 59·3 59·5 61·29
Oxygen	1	8	40 40·7 40·5 38·71
<hr/>								
Magnesia	1		20		100	100·0	100·0	100·00

Native Hydrate of Magnesia. This mineral was first discovered by Dr. Bruce, in the serpentine rocks of Hoboken, in New Jersey; it has also been found by Dr. Hibbert, in a vein traversing serpentine, at Swinanness in Unst, one of the Shetland Isles. It has a very pale greenish hue, and a soft lamellar texture; sp. gr. 2·3. Sometimes it forms acicular crystals and six-sided prisms. It consists (like the artificial,) of

						Bruce.	Fyfe.	Stromeyer.
Magnesia	1	20	69 70 69·75 68·35
Water	1	9	31 30 30·25 30·90
<hr/>								
Native hydrate of magnesia	1		29		100	100	100·00	99·25

CHLORIDE OF MAGNESIUM, MgCl , may be obtained, (1,) by passing chlorine or hydrochloric acid over red-hot magnesia; in the former case oxygen, and in the latter water, is evolved. A little charcoal, intimately mixed with the magnesia, facilitates the action. Bussy mixes the magnesia with its weight of starch, and forms it into a paste with water, which he heats in a covered crucible, so as to form a carbonaceous mass; this is introduced into a slightly-inclined red-hot porcelain tube, and dry chlorine passed over it: the chloride of magnesium then flows from the tube. (2.) By heating a mixture of 1 part of magnesia and 2 of sal-ammoniac in

a glass retort gradually to redness; or by Liebig's method, which consists in evaporating a solution of equal parts of hydrochlorate of ammonia and hydrated chloride of magnesium, and heating the dry residue in a platinum vessel till the hydrochlorate of ammonia is expelled and the mass fuses. *Chloride of magnesium* forms a lamellar white crystalline mass, which evolves heat when acted on by water. This chloride cannot be obtained by merely evaporating its aqueous solution to dryness in an open vessel, for in that case hydrochloric acid escapes, and magnesia remains. Chloride of magnesium is very deliquescent; it is soluble in about half its weight of water, and twice its weight of alcohol. It consists of

Magnesium	1	12	25
Chlorine	1	36	75
<hr/>					
Chloride of magnesium	1		48		100

When solution of chloride of magnesium is concentrated by evaporation, and exposed to a cold atmosphere, it yields prismatic hydrated crystals, deliquescent, very soluble in water and alcohol, and of a bitter and biting taste. This salt was formerly termed *muriate of magnesia*; it is found in a few saline springs, and in the water of the ocean, forming the principal ingredient in the liquid which remains after the separation of sea-salt, and which is usually called *bittern*. The above-mentioned crystals consist of

Chloride of magnesium	1	48	47.2
Water	6	54	52.8
<hr/>					
Crystals of hydrated chloride of magnesium	1		102		100.0

SEA-WATER. Chloride of sodium is, as already stated, the most abundant ingredient in the waters of the ocean; it constitutes about two-thirds of the whole saline contents; the magnesian salts are, however, very characteristic of sea-water, and confer upon it many of its peculiarities, such especially as its bitter flavor and clamminess.

The average specific gravity of *sea-water* is 1.026 or 1.028, and of its saline contents 3.5 *per cent.*: it freezes at about 28.5°: it does not appear materially to differ in composition in different latitudes, provided it be taken from a sufficient depth. Near the mouths of rivers, and in the vicinities of melting ice or snow, its composition will of course vary. Traces of chloride of potassium, and of iodine and bromine, may also be found in it; and, according to Dr. Marcet (*Phil. Trans.*, 1819 and 1822), of double sulphate of magnesia and potassa, and of hydrochlorate of ammonia. He has also detected in it a minute portion of carbonate of lime. In respect to the general constitution of sea-water, it appears from Marcet's researches, (1.) That the southern ocean contains more salt than the northern, in the ratio of 1.02919 to 1.02757. (2.) That the mean specific gravity of sea-water near the equator is 1.02777, or intermediate between that of the northern and southern hemispheres. (3.) That there is no notable difference in sea-water under different meridians. (4.) That there is no satisfactory evidence that the sea at great depths is more salt than at the surface. (5.) That the sea in general contains most salt where it is deepest and most remote from land, and that its saltness is always diminished in the vicinity of large masses of ice. (6.) That

small inland seas, though communicating with the ocean, are less salt than the ocean. (7.) That the Mediterranean contains rather larger proportions of salt than the ocean. (PROUT, *Bridgewater Treatise*.) According to Pfaff, 10,000 parts of the water of the Mediterranean contain 410 grains of solid matter; of the English Channel 380 grs. The following are their analyses. (*Phil. Mag.*, July, 1839.)

	Mediterranean. (LAURENS.)	English Channel. (SCHWEITZER.)
Water	959·26	964·74372
Chloride of sodium	27·22	27·05948
„ potassium	0·01	0·76552
„ magnesium.....	6·14	3·66658
Bromide of magnesium	—	0·02929
Sulphate of magnesia	7·02	2·29578
„ lime	0·15	1·40662
Carbonate of lime (and magnesia) ...	0·20	0·03301
	1000·00	1000·00000

According to these analyses it will be observed that the Mediterranean contains much more sulphate of magnesia and much less sulphate of lime than the Channel: traces of iodine and of ammonia were also detected in it.

CHLORIDE OF MAGNESIA. HYPOCHLORITE OF MAGNESIA. The fluid obtained by condensing chlorine in a mixture of magnesia and water, was recommended by Davy (*Elem. of Chem. Phil.*) for delicate bleaching operations, but has not been generally employed.

CHLORATE OF MAGNESIA, MgO, ClO_5 , is obtained by mixing a solution of fluosilicate of magnesia with a hot saturated solution of chlorate of potassa as long as a precipitate falls. (BERZELIUS.) When formed by saturating chloric acid with carbonate of magnesia, it is bitter, difficultly crystallizable, deliquescent, and very soluble in water and alcohol. From the analysis of Chenevix (*Phil. Trans.*, 1802), the crystals appear to contain 2HO . According to Wächter they contain 6HO , fuse at 104° , and are entirely decomposed at 248° .

PERCHLORATE OF MAGNESIA, MgO, ClO_7 , forms deliquescent prismatic crystals, soluble in alcohol. (SERULLAS.)

AMMONIO-CHLORIDE OF MAGNESIUM is a crystallizable salt soluble in 10 parts of water at 60° . (FOURCROY, *Ann. de Chim.*, iv. 215.)

POTASSIO-CHLORIDE OF MAGNESIUM may, by very careful evaporation, be obtained in rhombic crystals; but the constitution of this salt is so delicate, that it is liable to be separated into chloride of potassium and of magnesium by water alone; and it is with certainty decomposed by alcohol, which takes up the magnesian chloride, and leaves the other undissolved. (MARCET, *Phil. Trans.*, 1822, p. 456.) The crystallized salt contains

Chloride of magnesium.....	2	96	34·28
Chloride of potassium	1	76	27·14
Water	12	108	38·58
Crystallized potassio-chloride of magnesium	1	280	100·00

The corresponding soda salt is $= \text{NaCl}, 2\text{MgCl} + 2\text{HO}$. (POGGIALE.)

IODIDE OF MAGNESIUM. MgI . When iodine is heated with magnesia and water, *iodide of magnesium* and *iodate of magnesia* are formed. By concentrating the solution, both salts are partly decomposed, and a brown flocculent *iodide of magnesia* falls (resembling kermes in appearance), which, when heated, loses part of its iodine, and is changed into a *sub-iodide*. (HENRY, *Elem. Chem.*, i. 593.) The hydrated iodide obtained by dissolving magnesia in hydriodic acid is very difficultly crystallized, and when heated gives off hydriodic acid and leaves magnesia.

IODATE OF MAGNESIA. Iodic acid forms no precipitate in solutions of magnesian salts: the crystallized iodate, $\text{MgO}, \text{IO}_5, 4\text{HO}$, is obtained by digesting magnesia in solution of iodic acid.

BROMIDE OF MAGNESIUM, MgBr , was obtained by Löwig by passing bromine vapor over red-hot magnesia mixed with a little charcoal: it is a white crystalline substance not volatile and requiring a red heat for fusion: the hydrated bromide (hydrobromate) is a bitter deliquescent salt, resolved, by heat and air, into magnesia and hydrobromic acid. It forms acicular prisms, very soluble in water and alcohol. It exists in sea-water and some saline springs. The formula of the hydrated crystals is $\text{MgBr}, 6\text{HO}$.

BROMATE OF MAGNESIA, MgO, BrO_5 , forms efflorescent octohedral crystals, soluble in 1.4 of water. (RAMMELSBERG, *Poggend.*, lii. 89.)

FLUORIDE OF MAGNESIUM, MgF , is obtained by digesting magnesia in hydrofluoric acid. Berzelius says that it is insoluble in water, and not decomposed at a red-heat. (*Lehrbuch.*)

NITRATE OF MAGNESIA, MgO, NO_5 , crystallizes with difficulty in rhomboidal prisms, deliquescent, and soluble in their weight of water. In pure alcohol this salt is nearly insoluble, but one part dissolves in about 9 of alcohol of the specific gravity .840. Its taste is cooling and bitter, and it is decomposed at a red-heat. It is sometimes found in crude nitre. The crystallized salt, according to Kirwan and Bergman, contains about 30 *per cent.* of water; according to Thomson, 6 atoms. According to Graham, 1 atom of water is essential to the constitution of this salt, so that when the crystals containing 6 atoms of water are highly heated, only 5 atoms go off, and 1 atom remains in combination; this monohydrate may be fused without decomposition; when intensely heated the salt loses both acid and water, and magnesia remains; Graham therefore represents this salt as $\text{MgO}, \text{NO}_5, \text{HO}, + 5\text{HO}$. On evaporating the alcoholic solution of nitrate of magnesia, a solid alcoate is formed, with which a portion of water is also probably associated.

AMMONIO-NITRATE OF MAGNESIA may be obtained, according to Fourcroy, by evaporating a mixed solution of nitrate of ammonia and nitrate of magnesia; it forms prismatic crystals, of a bitter acrid taste, soluble in about 11 parts of water at 60° , and less deliquescent than their component salts separately. (*Ann. de Ch.*, iv. 215.) Berzelius admits the existence of this salt, but Graham did not succeed in forming it, or any other double nitrate.

SULPHURET OF MAGNESIUM. MgS . Sulphur and magnesia do not appear to form a complete sulphuret, for when melted together the compound does not dissolve in water; and when heated, the sulphur burns off. Nor can a sulphuret of magnesium be obtained by heating the metal with sulphur. (LIEBIG.) Berzelius states that sulphate of magnesia decomposed by an aqueous solution of sulphuret of barium yields a precipitate of sulphate of baryta and a solution of sulphuret of magnesium. According to Berthier, when sulphate of magnesia is intensely heated in a crucible lined with charcoal, a sulphuret of magnesium is formed; but when the charcoal is mixed with the sulphate, sulphur is evolved and magnesia only remains. (*Ann. Ch. et Ph.*, xxii. 236.) Hydrogen passed over sulphate of magnesia at a high temperature would also probably give this sulphuret.

Sulphuretted hydrogen gas passed through water holding hydrate of magnesia in suspension slowly dissolves it: by evaporation in vacuo sulphuretted hydrogen escapes and hydrosulphuret of magnesia falls: at a boiling heat the whole of the sulphuretted hydrogen is dissipated, and magnesia remains. (BERZELIUS.)

HYPOSULPHITE (DITHIONITE) OF MAGNESIA, $\text{MgO}, \text{S}_2\text{O}_2$, may be formed by boiling sublimed sulphur in solution of sulphite of magnesia; it is bitter, very soluble, but not deliquescent. Being more soluble in hot than cold water, it readily crystallizes as its solution cools; when heated, sulphur escapes, but the salt is not very combustible. (HERSCHEL.) The crystallized salt obtained by evaporation in vacuo forms permanent rectangular prisms, easily soluble in water, from which alcohol throws it down in the form of an oily fluid. (RAMMELSBERG, *Poggend.*, lvi. 303.) The crystals consist of

						Rammelsberg.
Magnesia	1	20	16.40 16.82
Hyposulphurous acid	1	48	39.34 39.23
Water	6	54	...	44.26 43.95
<hr/>						
Crystallized hyposulphite of magnesia	1		122		100.00	100.00

SULPHITE OF MAGNESIA, MgO, SO_2 , is prepared by passing sulphurous acid through water containing diffused magnesia. It forms tetrahedral crystals soluble in 20 parts of water at 60° , of a sweetish and sulphurous taste; they become opaque in the air, but are very slowly converted into sulphate: when in solution, however, this change soon ensues. When heated, this salt softens and acquires the consistence of gum, losing 0.45 of its weight; at a high heat the acid is disengaged, and pure magnesia remains. (FOURCROY and VAUQUELIN.)

AMMONIO-SULPHITE OF MAGNESIA may be obtained by mixing the solution of the two salts, or by saturating acid sulphite of magnesia with ammonia. It forms transparent difficultly-soluble crystals. (FOURCROY and VAUQUELIN.)

HYPOSULPHATE (DITHIONATE) OF MAGNESIA, $\text{MgO}, \text{S}_2\text{O}_5$, is difficultly crystallizable in hexagonal prisms, intensely bitter, fusible in their water of crystallization, very soluble in water, but not deliquescent. It is formed by mixing the solutions of sulphate of magnesia and hyposulphate

of baryta, and appears from Heeren's analysis (*Poggend.*, vii. 179), to consist, when crystallized, of

Magnesia	1	...	20	...	13·70
Hyposulphuric acid	1	...	72	...	49·31
Water	6	...	54	...	36·99
<hr/>					
Crystallized hyposulphate of magnesia	1		146		100·00

SULPHATE OF MAGNESIA, MgO, SO_3 , is a commonly-occurring salt, much used in medicine as an aperient. When concentrated sulphuric acid is poured upon magnesia, intense heat is produced, and sometimes light. If the acid be dilute, and poured upon carbonate of magnesia, the latter is slowly dissolved with effervescence; and, upon evaporating the filtered solution, crystals of sulphate of magnesia may be obtained.

The commercial demands for sulphate of magnesia are chiefly supplied from two sources, namely, sea-water, and magnesian limestone. When sea-water is resorted to, the greater part of the common salt is first removed by evaporation, and the remaining *bittern*, consisting chiefly of a solution of chloride of magnesium and sulphate of magnesia, is boiled down with the addition of sulphuric acid, by which the chloride is ultimately decomposed and converted into sulphate. Or the bittern may be decomposed by hydrate of lime, which is mixed with it in tanks, and the resulting precipitate is afterwards treated by sulphuric acid, by which sulphate of magnesia and sulphate of lime are obtained. When magnesian limestone is used as a source of sulphate of magnesia, it is calcined and reduced to powder by sprinkling it with water; it is then diffused through water and sulphuric acid is added, and as sulphate of magnesia is so much more soluble than sulphate of lime, it is easily separated. A solution of sulphate of lime may also be decomposed by carbonate of magnesia, as is sometimes seen, where water holding sulphate of lime in solution filters through strata of magnesian limestone.

The sulphate of magnesia from bittern is generally preferred as a source of magnesia, or carbonate of magnesia, in consequence of the absence of iron, traces of which are always discoverable in the sulphate obtained from the magnesian limestones; but as the latter is free from chloride of magnesium, and consequently not deliquescent, and may be obtained very nearly pure, it is preferred for general medical uses. Crude sulphate of magnesia may be purified by exposing it to a dull red heat, dissolving it in water, boiling it with the addition of calcined magnesia, filtering, and crystallizing. (GMELIN.)

There are some saline springs or mineral waters in which sulphate of magnesia is the leading ingredient, as those of Seidlitz, Seydschutz, Egra, and formerly those of Epsom in Surrey, whence the name of *Epsom salt*: it is also largely obtained in some alum works: it not unfrequently occurs as a fine capillary incrustation upon the damp walls of cellars and new buildings; and it has been found *native*, constituting the *hair salt* of mineralogists.

Hydrated sulphate of magnesia, $\text{MgO}, \text{SO}_3, 7\text{HO}$, crystallizes (see fig. 10, p. 7) in four-sided prisms with reversed dihedral summits, or four-sided pyramids. They refract double. (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 40.) Their density is 1·7. Exposed to the air, it has, when pure, a slight tendency to efflorescence, but the salt of commerce is often

deliquescent from the presence of a little chloride of magnesium. Its taste is saline and bitter. The crystals are soluble in about their own weight of water at 60° , and in three-fourths their weight of boiling water; or, 100 parts of water at 32° dissolve 25·76 parts of the anhydrous salt, and for every degree above that temperature they take up 0·26564 parts additional. (GAY LUSSAC.) It is much more soluble in hydrochloric acid than in water. When exposed to heat the crystals readily lose 6 equivalents of water of crystallization, but retain 1 equivalent more obstinately. At a red-heat this salt becomes anhydrous, and at a higher temperature it runs into a white enamel. The anhydrous salt regains water from the atmosphere, and when sprinkled with water evolves much heat. Its sp. gr. is 2·6.

The aqueous solution of sulphate of magnesia furnishes a precipitate of hydrated carbonate upon the addition of carbonate of potassa, or of soda, but carbonate of ammonia does not even render it turbid, unless heat be applied, in which case a precipitate is also thrown down. The alkaline bicarbonates occasion no precipitate when added to cold solution of sulphate of magnesia, but after some hours crystals of hydrated carbonate of magnesia are deposited. A dilute solution of sulphate of magnesia is not precipitated by oxalate of ammonia.

The sulphate of magnesia of commerce is occasionally adulterated with small crystals of sulphate of soda; the fraud is detected by the inferior weight of the precipitate occasioned by adding carbonate of potassa; or the solution of the mixed salt may be precipitated by baryta-water and filtered; the excess of baryta is then removed by carbonate of ammonia, and filtering, and the liquor when evaporated leaves carbonate of soda. If a solution of sulphate of magnesia containing sulphate of soda be shaken for some time with carbonate of baryta, the liquor becomes strongly alkaline from the evolution of soda. Anhydrous sulphate of magnesia consists of

				Henry.	Gay Lussac.	Ber- zelius.	Wenzel.
Magnesia.....	1	20	33·33	32·14	33	34	35·5
Sulphuric acid	1	40	66·67	67·86	67	66	64·5
<hr/>							
Anhydrous sulphate of magnesia	1	60	100·00	100·00	100	100	100·0

And the common *crystallized* salt contains, according to Graham, 1 atom of constituent water and 6 of water of crystallization, it being represented by $\text{MgO}, \text{SO}_3, \text{HO} + 6\text{HO}$. The proximate elements of the crystals are

					Gay Lussac.	Wenzel.
Magnesia	1	20	16·26	16·04	16·86	
Sulphuric acid	1	40	32·52	32·53	30·64	
Water	7	63	51·22	51·43	52·50	
<hr/>						
Crystallized sulphate of magnesia	1	123	100·00	100·00	100·00	

There are other hydrates of this salt: namely a *monohydrate* $[\text{MgO}, \text{SO}_3, \text{HO}]$, obtained by heating the common crystals to 270° . A *binhydrate*, $[\text{MgO}, \text{SO}_3, 2\text{HO}]$, formed by drying the common crystals at 212° in vacuo over sulphuric acid. (GRAHAM.) A *hexhydrate* $[\text{MgO}, \text{SO}_3, 6\text{HO}]$, in opaque crystals resembling borax, by evaporating the solution of the sulphate till a pellicle forms, and setting it aside to crystallize very slowly in a warm place. (HAIDINGER.) And lastly, when a satu-

rated solution of the common sulphate is cooled below 32°, it forms ice, and crystals which may be separated by thawing at 32°, and which are either small and opaque, or large and transparent = $MgO,SO_3,12HO$. Above 32° they lose water but retain their form, and pass into opaque crystals with 7 atoms of water. (FRITZSCHE.)

AMMONIO-SULPHATE OF MAGNESIA. $NH_4O,MgO,2SO_3,6HO$, may be obtained by mixing solution of sulphate of ammonia with solution of sulphate of magnesia; if the solutions are concentrated, it falls as a white crystalline powder; or by pouring ammonia into a solution of the sulphate of magnesia, in which case, part only of the magnesia is thrown down, the remainder forming, with the sulphate of ammonia, this triple salt. It crystallizes in oblique rhombic prisms. (BROOKE, *Ann. of Phil.*, 2nd Series, vii. 117.) Its sp. gr. is 1.72. The crystals contain

					Fourcroy.	
Ammonia.....	1	17	9.44	
Magnesia	1	20	11.11	
Sulphuric acid....	2	80	44.45	
Water	7	63	35.00	
<hr/>					<hr/>	
Crystallized	1		180		100.00	
					Dry	100

SULPHATE OF POTASSA AND MAGNESIA. $KO,MgO,2SO_3,6HO$, forms rhomboidal crystals, scarcely more soluble than sulphate of potassa, and of a bitter taste. This salt appears to exist in sea-water. (MARCET.) It may be obtained by evaporating a mixed solution of 1 atom of each of the sulphates, in hydrated crystals isomorphous with the ammonio-sulphate of magnesia. According to Graham's view of the constitution of these sulphates, the atom of *constituent* water of the sulphate of magnesia is in this salt replaced by an atom of sulphate of potassa; its components being

						Mitscherlich.
Potassa	1	48	23.76 23.46
Magnesia	1	20	9.90 9.94
Sulphuric acid	2	80	39.60 39.76
Water	6	54	26.74 26.84
<hr/>					<hr/>	
					1	202
					100.00	100.00

SULPHATE OF SODA AND MAGNESIA. $NaO,MgO,2SO_3,6HO$, forms truncated rhombic crystals, soluble in about 5 parts of water at 60°; it was first examined by Link, and afterwards by Murray. (*Edin. Phil. Trans.*, viii.) In this salt an atom of sulphate of soda appears to replace the *constituent* atom of water in the sulphate of magnesia; for its proximate elements are

						Murray.
Sulphate of soda	1	72	38.7 39
Sulphate of magnesia	1	60	32.3 32
Water	6	54	29.0 29
<hr/>					<hr/>	
					1	186
					100.0	100

PHOSPHURET OF MAGNESIUM has not been examined.

HYPOPHOSPHITE OF MAGNESIA. $MgO,PO,8HO$, may be obtained by boiling oxalate of magnesia for a long time with hypophosphite of lime,

filtering, and carefully evaporating the liquid; or by the action of hypophosphite of baryta on sulphate of magnesia. It crystallizes in efflorescent octohedra, containing 55 *per cent.* of water of crystallization; when this salt is heated it gives off water and phosphuretted hydrogen, and phosphate of magnesia remains. (H. ROSE.) Heated to 212°, it loses 5 equivalents of water. (WÜRTZ.)

PHOSPHITE OF MAGNESIA. MgO,PO_3 , is obtained by boiling magnesia in the aqueous phosphorous acid, and evaporating in vacuo; it forms crystalline films containing more water of crystallization than the phosphites of baryta or lime: when decomposed by heat it yields hydrogen and phosphuretted hydrogen, and a yellowish-brown phosphate of magnesia remains. An *ammonio-phosphite of magnesia* may be formed, which is crystallizable, and difficultly soluble.

PHOSPHATES OF MAGNESIA. 1. *Tribasic phosphates.* *a. Anhydrous tribasic phosphate.* $3MgO,cPO_5$. A solution of sulphate of magnesia is precipitated by tribasic phosphate (subphosphate) of soda. Dried at 100° this salt retains 5 atoms of water: at a white heat it fuses into a clear glass easily soluble in acids: in this state it consists of

Magnesia	3	60	45·45
Phosphoric acid.....	1	72	54·55
<hr/>					
Anhydrous tribasic phosphate of magnesia	1		132		100·00

Dried at 100° it is $3MgO,cPO_5,+5HO$: its constituents being

Magnesia	3	60	33·89
Phosphoric acid	1	72	40·67
Water	5	45	25·44
<hr/>					
Hydrated tribasic phosphate of magnesia	1		177		100·00

β. Tribasic phosphate of magnesia and water. $2MgO,HO,cPO_5+14HO$. This phosphate is formed by mixing a solution of 2 parts of common crystallized sulphate of magnesia in 32 of water, with a solution of 3 parts of common crystallized phosphate of soda in 32 of water: after 24 hours acicular crystals are deposited, having the above formula, or according to Graham, being $HO,2MgO,PO_5+2HO+12HO$. (*Phil. Trans.*, 1837.) They effloresce in the air, and slowly dissolve in 322 parts of cold water: at 120° this solution becomes turbid, and at 212° milky, from the separation of a part of the salt in a bulky uncrystalline state, so that in the boiling solution 498 parts of water only hold 1 part of the salt: on cooling, a part of the precipitated salt again slowly dissolves. This salt is much more soluble in very dilute acids, and is not then affected by boiling. The composition of this salt with its atom of constituent water is

Magnesia	2	40	33·05
Water	1	9	7·45
Phosphoric acid.....	1	72	59·50
<hr/>					
Tribasic phosphate of magnesia and water.....	1		121		100·00

And in its ordinary state of hydrated crystals it consists of

Magnesia	2	40	16·19
Basic water	1	9	3·64
Phosphoric acid	1	72	29·14
Water of crystallization	14	126	51·03
<hr/>					
Crystallized tribasic phosphate (common phosphate) of magnesia and water	1		247		100·00

On heating magnesia or any phosphate of magnesia with excess of glacial phosphoric acid, a dense granular insoluble phosphate may be obtained= $2\text{MgO} + 3\text{PO}_5$. (GREGORY.)

2. *Pyrophosphate of Magnesia. Bibasic Phosphate of Magnesia*, $2\text{MgO}, 6\text{PO}_5$, is formed by the ignition of the preceding salt, or of the tribasic ammonio-magnesian phosphate; it is a transparent glass, composed of

Magnesia	2	40	35·71
Phosphoric acid.....	1	72	64·29
<hr/>					
Pyrophosphate of magnesia	1		112		100·00

3. *Monobasic Phosphate. Metaphosphate of Magnesia*. $\text{MgO}, a\text{PO}_5$. Metaphosphate of soda added to acetate of magnesia gives a soft viscid precipitate, but not with sulphate of magnesia. (GRAHAM.)

PHOSPHATE OF AMMONIA AND MAGNESIA. This salt, which also belongs to the class of *tribasic phosphates*, is produced when an ammoniacal salt, or pure ammonia, is added to a mixture of common phosphate of soda with any magnesian salt. Thus on adding ammonia or carbonate of ammonia to a mixed solution of phosphate of soda and sulphate of magnesia, the ammonio-magnesian phosphate falls in the form of a white granular or crystalline precipitate, insoluble in the liquid from which it is thrown down, but sparingly soluble in pure water, so that it cannot be washed upon the filter without sensible loss. It is readily soluble in the greater number of diluted acids. When its solution in aqueous carbonic acid is exposed to the air it slowly forms a superficial crystalline film as the carbonic acid escapes; and if bicarbonate of ammonia be used in its formation it falls slowly, but its appearance is accelerated by drawing lines with a glass rod upon the surface of the glass or basin containing the mixed solutions, when the double phosphate presently appears upon those lines. This method of recognising the presence of magnesia was first suggested by Wollaston; and indeed, the formation of this double salt is the readiest test of magnesia which we possess. The composition of this salt has been variously stated, especially as regards the proportion of ammonia and of water which it retains under various modes of drying. According to Graham, when dried at 65° , its formula is $\text{NH}_4\text{O}, \text{MgO}, \text{PO}_5 + 2\text{HO} + 10\text{HO}$. 10 atoms of its water may be expelled without any loss of ammonia. If it be rapidly dried and then raised to a red-heat, it appears to burn like tinder, and leaves a residue of *pyrophosphate of magnesia*, which contains nearly 36 per cent. of magnesia. Its composition may be represented as follows, when dried at 65° .

Ammonia	1	17	6·91
Magnesia	2	40	16·26
Phosphoric acid.....	1	72	29·26
Water	13	117	47·57
<hr/>					
Ammonio-magnesian phosphate	1		246		100·00

The ammonio-magnesian phosphate is deposited from human urine, often in the form of white sand, or as a superficial crystalline film, especially in cases where the natural acidity of the urine is diminished by diet, medicine, or morbid action, constituting what has been termed the phosphatic diathesis: it frequently forms urinary calculi both in the human subject and in quadrupeds, and it commonly occurs in intestinal concretions. The presence of phosphate of magnesia in the husk of grain, in the potato, and other plants, is important to the agriculturist, and shows why phosphoric acid and magnesia are contained in fertile soils: its existence in urine and most animal manures contributes therefore to their efficacy: it has been said especially to promote the growth of potatoes. “In turf ashes, which often prove a valuable manure, it is met with in appreciable quantity, and their beneficial operation has been in part attributed to this phosphate.” (JOHNSTON.) It may be detected in considerable quantity in good malt liquor.

CARBONATE OF MAGNESIA. *Magnesia alba*. This term is generally applied to the white precipitate obtained by adding carbonate of soda or potassa to a solution of sulphate of magnesia, and carefully edulcorating and drying the precipitate; it is usually obtained from boiling solutions, and great attention should be paid to the purity of the water employed in washing the precipitate, and to the method of drying it. It has been repeatedly analyzed, and the following are some of the results:—

	Kirwan. Bergman.			Dalton and Henry.		Klaproth.	Bucholz. hot ppt. cold ppt.			Berzelius.			
Magnesia.....	45	45	43	40	42	33	41·60 to 43·2
Carbonic acid	34	25	40	33	35	32	36·58 to 36·4
Water.....	21	30	17	27	23	35	21·82 to 20·4
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	100		100		100		100		100		100		100·00 100·0

Different views have been entertained of the atomic constitution of this compound: it probably varies with the mode of precipitation, and the temperature of the solutions, and certainly with the mode of drying; it most usually approaches to 5 atoms of magnesia, 4 of carbonic acid, and 6 of water:

Magnesia	5	100	41·32
Carbonic acid	4	88	36·36
Water	6	54	22·32
<hr/>					
Magnesia alba	1		242		100·00

This composition may be represented by the formula 4[MgO,CO₂,HO] + MgO,2HO=4 atoms of monohydrated carbonate in combination with 1 atom of binhydrate of magnesia.

Two kinds of carbonate of magnesia are kept in the shops, the *light* and the *heavy*: they are prepared as follows. (PEREIRA, *Elements of Mat Med.*, 363.) “For *heavy* magnesia, add 1 volume of a cold saturated solution of carbonate of soda to a boiling mixture of 1 volume of a saturated solution of sulphate of magnesia and 3 volumes of water: boil until effervescence has ceased, constantly stirring with a spatula. Then dilute with boiling water, set aside, pour off the supernatant liquor, and wash the precipitate with hot water on a linen cloth; afterwards dry it

by heat in an iron pot. *Light* magnesia is prepared by employing dilute solutions of the sulphate of magnesia and carbonate of soda. If no heat be used it is apt to be gritty. A heavy and gritty magnesia is prepared by separately dissolving 12 parts of sulphate of magnesia and 13 parts of crystallized carbonate of soda in as small a quantity of water as possible, mixing the hot solutions, and washing the precipitate." According to Fownes, the heavy and light varieties do not differ in composition. (*Pharm. Jour.*, III. 480.)

Durand gives the following as the mode of preparing the light cubes of magnesia often met with in commerce: A solution of 100 parts of sulphate of magnesia in 100 of water is put into a vat heated by steam, and a solution of 125 parts of crystallized carbonate of soda is quickly stirred into it, and the temperature raised to 176° to expel carbonic acid, which holds some of the magnesia in solution; the liquor is then decanted off the precipitate, and this is washed three times, by subsidence and decantation, with luke-warm water free from salts of lime: it is then transferred to linen strainers, where it is allowed to drip 24 to 48 hours, and is transferred in a wet state to cubical boxes without bottoms, placed upon a table of plaster or porous stone, so as quickly to absorb the water; after a time, the boxes are turned upside down, so as to present the upper side of the magnesia to the absorptive surface, and the drying is ultimately completed in warm rooms. (*Ann. Ch. et Ph.*, Liv., 312.)

There are other processes than those above mentioned by which the carbonate of magnesia of commerce is procured, such as by decomposing the *bittern* of the sea-salt works, by magnesian limestone, or by crude carbonate of ammonia, produced by the distillation of bone; in the latter case sulphate and hydrochlorate of ammonia and carbonate of magnesia result; the solution of the ammoniacal salts is evaporated to dryness and sublimed with chalk; carbonate of ammonia is thus reproduced for the decomposition of a second portion of bittern, and so on. A mode of separating magnesia from the magnesian limestone of Durham has been adopted by Mr. Pattinson of Gateshead, which consists in calcining it at a dull red heat, by which the magnesian carbonate only is decomposed; the calcined stone is then diffused through water, and subjected to the action of carbonic acid under pressure, by which the magnesia only is dissolved, and is afterwards obtained by rapidly boiling down the solution. (*Pharm. Journ.*, III. 424.)

When a current of carbonic acid is passed through a mixture of water and carbonate of magnesia, a clear solution is obtained which has a bitter taste, and which, when surcharged with carbonic acid, affords a useful medicinal preparation. But a solid or crystallized bicarbonate of magnesia cannot be obtained, and the crystals which are deposited when this solution is left to spontaneous evaporation, and which are oblique rhombic prisms (BROOKE, *Ann. Phil.*, 2nd Series, vi. 375), are hydrated carbonate of magnesia, composed of

						Berzelius. Henry.	
Magnesia	1	20	29	29.6	30		
Carbonic acid.....	1	22	32	31.5	30		
Water	3	27	39	38.9	40		
<hr/>							
Crystallized hydrated carbonate of magnesia	1	69	100	100.0	100		

When these crystals of hydrated carbonate are put into cold water

they are decomposed, carbonate of magnesia is dissolved, and a subcarbonate is deposited. Boiling water produces the same precipitate, but carbonic acid is evolved, and nothing remains in solution; in this case the precipitate is *magnesia alba*. (BERZELIUS.) Exposed to a dry air they effloresce, and lose 2 equivalents of water. (GRAHAM.)

Berzelius and Fritzsche have described other hydrated carbonates of magnesia, their composition apparently depending upon the relative proportions of the precipitants, and the temperature of desiccation—namely, $(3\text{MgO}, 2\text{CO}_2, 3\text{HO},)$ $(4\text{MgO}, 3\text{CO}_2, 4\text{HO},)$ $(5\text{MgO}, 4\text{CO}_2, 5\text{HO},)$ which is *magnesia alba* less an atom of water, $(\text{MgO}, \text{CO}_2, 3\text{HO},)$ and $(\text{MgO}, \text{CO}_2, 5\text{HO},)$ (GMELIN. *Handbuch*.)

Native Carbonate of Magnesia has been found in Piedmont and Moravia, constituting the mineral called *magnesite*. It has also been found at Hoboken, in North America, in veins in a serpentine rock, accompanying the *native hydrate*. It is generally white and friable, and in some places in fine acicular crystals. A variety of *native carbonate of magnesia* brought from the East Indies by Mr. Babington, has been described and analyzed by Dr. Henry. (*Ann. of Phil.*, i. 254.) It is white, massive, hard, of a conchoidal fracture, and translucent at the edges; specific gravity, 2·6. It slowly dissolves in acids, and is composed of 1 atom of magnesia + 1 atom carbonic acid.

CARBONATE OF AMMONIA AND MAGNESIA. When 3 parts of sesquicarbonate of ammonia and 1 of sulphate of magnesia are dissolved in water, transparent rhombohedral crystals are after a time deposited, constituting this double salt. They are soluble without decomposition in boiling water, but continued boiling renders the solution turbid. At a red-heat their carbonic acid, ammonia, and water are volatilized, and magnesia amounting to 15·6 *per cent.* remains. (GUIBOUT.) When a saturated solution of magnesia in carbonic acid is mixed with a solution of carbonate of ammonia, an abundant crystalline precipitate of the ammonio-magnesian carbonate ensues= $(\text{MgO}, \text{CO}_2; \text{NH}_4\text{O}, \text{CO}_2; 4\text{HO},)$ This salt is not soluble without decomposition. (FAVRE. *Ann. Ch. et Ph.*, Apr., 1844.)

CARBONATE OF POTASSA AND MAGNESIA. When excess of bicarbonate of potassa is mixed with chloride of magnesium no precipitation ensues, but in a few days crystals are formed, of an alkaline taste, which are decomposed by hot water. They may be regarded as a hydrated compound of 1 atom of bicarbonate of potassa + 2 atoms of carbonate of magnesia, for they consist of

						Berzelius.
Potassa	1	48	18·7 18·28
Magnesia	2	40	15·6 15·99
Carbonic acid	4	88	34·2 34·49
Water	9	81	31·5 31·24
	—		—		—	—
	1		257		100 0	100·00

According to Graham, this salt loses 8 equivalents of water at 212° , retaining a single basic equivalent.

CARBONATE OF SODA AND MAGNESIA is formed as the triple potassa salt, by bicarbonate of soda; but it is not so easily decomposed; and,

accordingly, when magnesia is precipitated by excess of carbonate of soda, a portion of the triple soda-salt is retained, and not easily washed away.

CARBONATE OF LIME AND MAGNESIA is the mineral known under the name of *bitter spar*; it has the primitive form of carbonate of lime, and consists of 1 atom of each of its component carbonates. *Dolomite*, or magnesian carbonate of lime, is similarly constituted, being $MgO,CO_2 + CaO,CO_2$. Some varieties of bitter spar and dolomite are also $= 3[CaO,CO_2] + 2[MgO,CO_2]$, and $2[CaO,CO_2] + [MgO,CO_2]$. The formula of *conite* is $CaO,CO_2 + 3[MgO,CO_2]$. (GMELIN. *Handbuch*.)

CYANIDE OF MAGNESIUM. $MgCy$, is formed when hydrated magnesia is dissolved in hydrocyanic acid; it is unknown in the solid form, being decomposed by heat and by carbonic acid during the evaporation of its solution.

SULPHOCYANIDE OF MAGNESIUM. $MgCsy$, is a very soluble, deliquescent, difficultly crystallized salt, formed by dissolving carbonate of magnesia in aqueous hydrosulphocyanic acid: the crystals include 4 atoms of water, and are soluble in alcohol.

MELLONIDE OF MAGNESIUM is gradually deposited in fine acicular crystals from a mixed solution of sulphate of magnesia and mellonide of potassium. (LIEBIG.)

BORATES OF MAGNESIA. Several of these salts have been described.

1. *Tribasic Borate*. $3MgO,BO_3$. Sulphate of magnesia precipitated by a solution of borax at a boiling heat, gives this compound: it should be well washed with cold water, in which it is very little soluble, and dried in vacuo over oil of vitriol; it is partially decomposed by long boiling in water. When heated to redness, it loses between 46 and 47 per cent. of water, its formula, as hydrate, being $3MgO,BO_3,9HO$. (RAMMELSBERG.)

2. *Neutral Borate*. MgO,BO_3 . A mixed solution of borax and sulphate of magnesia (heated till it became turbid, and then suffered to clear again on cooling,) was kept at a low temperature for some months, (often below 32°); it yielded groups of acicular crystals containing 16.7 of magnesia, 25 boracic acid, and 58.3 of water, per cent. (WÖHLER.)

3. *Boracite*. $3MgO,4BO_3$, or $2[MgO,BO_3] + [MgO,2BO_3]$. This is a scarce mineral from Lüneburgh. Its primitive form is the cube, but the edges and angles are generally replaced by secondary planes, and four of the angles are always observed to present a greater number of facets than the other four: these crystals become electric by heat, the most complex angles being rendered positive, and the simplest negative. It sometimes contains lime. Its sp. gr. is 2.95: it is difficultly fusible before the blow-pipe, insoluble in water, and slowly soluble in acids. It consists of

Arfwedson. Rammelsberg. Stromeyer.											
Magnesia	3	60	30	30.3	30.75	33
Boracic acid	4	140	70	69.7	69.25	67
<hr/>										<hr/>	
Boracite	1		290		100		100.0		100.00		100

4. *Terborate*. $MgO,3BO_3,8HO$. Obtained by boiling together in

water excess of hydrate of magnesia with boracic acid, filtering and evaporating for crystallization: it forms granular crystals and crusts, soluble in 75° of cold water. (RAMMELSBERG.)

5. *Superborate*. $\text{MgO}, 6\text{BO}_3, 18\text{HO}$, is occasionally formed by boiling carbonate of magnesia with boracic acid along with the preceding salt: it is a granular powder. (RAMMELSBERG, *Poggend.*, xlix., 445.)

FLUOBORATE OF MAGNESIA. MgF, BF_3 , yields large prismatic crystals, very soluble in water. (BERZELIUS. *Lehrbuch*.)

THE SALTS OF MAGNESIA, are mostly soluble in water and bitter: they are all soluble in hydrochloric acid; their aqueous solutions are precipitated by potassa and soda, the precipitate being soluble in hydrochloric, nitric, and sulphuric acids, and in hydrochlorate, nitrate, and sulphate of ammonia. Ammonia only throws down part of the magnesia, and forms a double salt, and carbonates of potassa and soda only throw down a part of the magnesia, except the solution be heated, when nearly the whole is precipitated. Sal-ammoniac redissolves the precipitate, and when previously added to the magnesian solution, no precipitate ensues on adding the alkaline carbonates, unless the liquor be heated. The bicarbonates of ammonia, potassa, and soda give no precipitate in magnesian solutions, except the liquor be boiled. Common phosphate of soda only precipitates concentrated magnesia solutions, but if ammonia or carbonate of ammonia be added, the magnesia is precipitated in the form of ammonio-magnesian phosphate. Moistened with nitrate of cobalt, and heated before the blow-pipe, the magnesian salts give pale rose-colored compounds: the tint is only distinct on cooling, and never very intense.

In quantitative analysis magnesia is almost always precipitated by a solution of phosphate of soda, to which ammonia or its carbonate have been previously added; it is collected and washed with the precautions above mentioned, and ignited so as to be weighed in the state of pyrophosphate. Every 100 parts of ammonio-magnesian phosphate, dried at 60° , indicate 16.26 of magnesia: every 100 parts of its residue, after ignition, indicate 35.7 parts of magnesia.

The separation of magnesia and lime is a problem of some importance in analytical chemistry, as they often exist together in the same mineral, more especially in the varieties of magnesian limestone. 1. Phillips (*Quart. Journ.*, vi. 317) proposes the following process:—"To the hydrochloric or nitric solution of lime and magnesia, add sulphate of ammonia in sufficient quantity; evaporate the mixture gradually to dryness, and then heat the residue to redness till it ceases to lose weight, by the volatilization of the hydrochlorate or nitrate of ammonia formed: note the weight of the mixed salt, reduce it to powder, and wash it with a saturated solution of sulphate of lime till all the sulphate of magnesia appears to be dissolved; dry the sulphate of lime left, and by deducting its weight from that of the mixed sulphates, the quantity of magnesia dissolved will appear." 2. Dissolve the two earths in hydrochloric acid in excess, and saturate the acid liquor by ammonia: then add oxalate of ammonia, and collect the precipitated oxalate of lime on a filter; the magnesia which is retained in the filtered liquor may be thrown down by phosphate of soda in the form of ammonio-magnesian phosphate, or the

solution may be evaporated to dryness, and the residue heated red-hot, so as to leave magnesia. 3. Evaporate the hydrochloric solution of the two earths to dryness, and expel the excess of acid from the residue, by heating in a platinum crucible: powdered chlorate of potassa is then added so long as the evolution of chlorine is perceived. On treating the residue with water, chloride of calcium and chloride of potassium are dissolved, and pure magnesia remains, which is separated upon a filter, washed, ignited, and weighed; the lime in the filtrate may be precipitated by oxalate of ammonia. (DOBEREINER.)

Separation of Magnesia from the Fixed Alkalis. Add subphosphate of ammonia to the solution to throw down the magnesia as ammonio-phosphate, and filter; add acetate of lead to the filtrate as long as it occasions any precipitate; filter again, and supersaturate the clear liquor with sulphuretted hydrogen; separate the sulphuret of lead, and evaporate the solution to dryness. The residue, consisting of acetates, may be converted by hydrochloric acid into chlorides of potassium and sodium, which may be dissolved in water, and chloride of platinum will then throw down the potassium, which may be estimated from the weight of the potassio-chloride.

MAGNESIAN MINERALS are often soft and apparently unctuous to the touch; they have seldom either lustre or transparency, and are generally more or less of a green color. *Steatite* or *soapstone*, *talc*, and *asbestos*, may be taken as instances. The *chrysolite*, however, contains more than half its weight of magnesia. The mineral called *bitter spar*, of which the finest specimens come from the Tyrol, contains 45 per cent. carbonate of magnesia, 52 carbonate of lime, and a little iron and manganese. Its primitive crystal is a rhomboid nearly allied to that of carbonate of lime; its angles being $106^{\circ} 20'$, and $73^{\circ} 80'$. It is generally of a yellowish color, and a pearly lustre; semi-transparent and brittle. A variety found at *Miemo* in Tuscany, has been called *Miomite*. The species of marble, termed *Dolomite*, found in the Alps, at Icolmkill in Scotland, and elsewhere, contains also a large quantity, generally 40 per cent. of carbonate of magnesia. The same may be said of the *magnesian limestone* of Derby and Nottingham: it is generally of a yellowish color, and less rapidly soluble in dilute hydrochloric acid than the purer limestone, whence the French have termed it *chaux carbonatée lente*. The lime which it affords is much esteemed for cements, but for agricultural purposes it is often mischievous, in consequence, probably, of its remaining caustic for a very long time, and injuring the young plant.

§ VIII. MANGANESE. Mn. 28.

THE common ore of manganese is the black, or *peroxide*, which is found in considerable abundance, and is, as a source of oxygen, of important use in the arts; traces of manganese also occur in a few animal products, and in the ashes of some vegetables, and it has been found in some spring waters. Attention was first directed to the black oxide of manganese by Scheele, in 1774, and shortly afterwards Gahn found that it contained a peculiar metal, which he called *Magnesium*, but which was afterwards termed *Manganese*.

In some respects manganese resembles the metals already described;

in others, it is eminently different. Like them, it has a powerful affinity for oxygen, speedily attracting it from air and water; and its oxides are difficult of decomposition: they have, however, nothing in common with alkaline bodies; and manganese, in its highest states of oxidizement, forms acids.

To obtain metallic manganese, *carbonate of manganese* mixed into a paste with oil, is subjected to heat gradually raised to redness, in a close vessel. The carbonaceous mixture thus obtained is then rammed into a good crucible filled up with charcoal-powder, and subjected for two hours to a white heat in a wind-furnace: a metallic button is thus obtained, which is manganese, containing a little carbon and silicium, from which it may be freed, according to Dr. John, by fusion with borax in a crucible coated with charcoal; it is doubtful, however, whether in this case it does not retain boron or sodium.

When *tartrate of manganese and potassa* is intensely heated in a wind-furnace, it furnishes globules of metallic manganese; and as this salt is easily obtained in a state of purity, its decomposition is perhaps the simplest process for obtaining the metal, care being taken to exclude foreign substances derivable from the fuel or crucible; but here again the presence of carbon and of potassium may be detected in the reduced metal, so that it is difficult to say whether manganese has ever been obtained in absolute purity.

Manganese appears as a grey metal; it has a granular and sometimes a slightly crystalline fracture: its specific gravity is 8.013 according to John, 7.05 according to Berthier, and 6.8 according to Bergman. The specific heat of a specimen of manganese, not however pure, but containing carbon, was, as determined by Regnault, $=0.14411$. When pure, it does not affect the magnetic-needle, but often does so from containing a trace of iron. (Berthier has stated that it is magnetic at very low temperatures, but Faraday could not observe this.) It is softer than iron, and admits of filing, yet brittle enough to be reduced into powder. It is best preserved in naphtha, for in the air it tarnishes and crumbles into grey powder; it undergoes the same change in water, with the evolution of hydrogen. It may also be conveniently kept in a glass tube hermetically sealed. When handled with moist fingers, it exhales a disagreeable odor, and when acted on by acids, the purest specimens hitherto obtained always afford traces of carbon; there are therefore considerable discrepancies in the accounts of the properties ascribed to this metal. (See *Carburet of Manganese*.)

The equivalent of manganese may be assumed as $=28$, (28 GMELIN. 27.7 TURNER.)

MANGANESE AND OXYGEN. There are five compounds of manganese and oxygen, three of which are oxides, and two acids; together with two intermediate oxides, namely, the red oxide, and the mineral called Varvicite. The formulæ of these oxides are as follows:

Protoxide.....	MnO
Sesquioxide (Deutoxide).....	Mn ₂ O ₃
Binoxide (Peroxide)	MnO ₂
Red oxide (Hausmannite).....	Mn ₃ O ₄
Varvicite	Mn ₄ O ₇
Manganic acid.....	MnO ₃
Permanganic acid	Mn ₂ O ₇

PROTOXIDE OF MANGANESE. MANGANOUS OXIDE, MnO , is obtained:

1. By passing a current of dry hydrogen over the pure deutoxide or peroxide of manganese, contained in a porcelain or iron tube, exposed to a heat gradually raised to bright redness: water is formed, and a dingy-green powder remains, which is the *protoxide*. It should be allowed to cool before removal from the tube, otherwise it is apt to absorb oxygen. The oxide obtained by igniting the protonitrate of manganese is recommended by Turner as best suited to this reduction, the native oxide, and especially the peroxide, being reduced with great difficulty. The reduction, he says, commences at a low red-heat, but a full red-heat is required for its completion.
2. By mixing the peroxide with half its weight of hydrochlorate of ammonia, and projecting the mixture in successive portions into a red-hot crucible; the product is lixiviated, and the solution of chloride of manganese, thus obtained, is decomposed by carbonate of potassa; the precipitated protocarbonate of manganese is then washed, dried, and exposed, out of the contact of air, to an intense heat: or it may be heated in a tube, through which a current of dry hydrogen is passed. In this process, so long as there is excess of the oxide, the manganese only is converted into chloride by the hydrochlorate of ammonia, and other metals that may be present are not rendered soluble.
3. By heating chloride of manganese to redness, with twice its weight of carbonate of soda; the resulting chloride of sodium is removed by washing from the residuary protoxide of manganese. The addition of a small quantity of hydrochlorate of ammonia in this process is useful to prevent the formation of any peroxide.

Protoxide of manganese is of a grey-green color, and when obtained by the action of hydrogen, and exposed to air before it is cooled, it acquires oxygen and is sometimes pyrophoric; obtained by the other processes it is not altered by mere exposure at common temperatures. Heated in the air it is converted into deutoxide; and at a temperature of about 600° burns sometimes like tinder. It is soluble in the dilute acids, and is the basis of the ordinary manganesian salts, which are isomorphous with the salts of mangnesia. When put into concentrated sulphuric acid, it evolves intense heat. Its solutions and salts are nearly colorless when pure, but often acquire a slightly pink hue, which has been ascribed to the presence of a minute quantity of manganic acid, "but as the color is not destroyed by sulphuretted hydrogen, it must be considered as a peculiar, although only occasional, character of manganese salts." (GRAHAM.) When ammonia is added to solutions of this oxide, the whole is not precipitated, but a double salt is formed, as with magnesia: thus $2[\text{MnO}, \text{SO}_3] + \text{NH}_3 = [\text{MnO}, \text{NH}_3, 2\text{SO}_3] + \text{MnO}$. If manganestic solutions contain silica, (as is often the case, and especially in the analysis of ores and minerals containing manganese,) the silica falls in combination with the oxide of manganese, when they are precipitated by an alkali; it may be separated by dissolving or digesting the moist precipitate in hydrochloric acid, evaporation to dryness, and washing. (BERZELIUS.) This oxide consists of

				Berzelius and			
				Forchammer.	Arfwedson.	Davy.	
Manganese	1	28	77.77	76.5	78.07	79	
Oxygen	1	8	22.23	23.5	21.93	21	
Protoxide of manganese....	1	36	100.00	100.0	100.00	100	

HYDRATED PROTOXIDE OF MANGANESE. When the solution of chloride of manganese is decomposed by a solution of potassa, a bulky white precipitate falls, which is *hydrated protoxide* of manganese, containing, according to Davy, 24 *per cent.* of water; it speedily becomes brown by exposure to air, absorbing oxygen and a little carbonic acid; and, when collected and washed upon a filter, it gradually becomes a hydrate of the sesquioxide. A similar change is immediately produced by solution of chlorine or chloride of lime, by which a hydrate of the sesquioxide, or perhaps of the binoxide, is formed. The recently precipitated and moist hydrate of the protoxide is soluble in ammonia, but not in potassa or soda.

SESQUIOXIDE OF MANGANESE. MANGANIC OXIDE. DEUTOXIDE OF MANGANESE. Mn_2O_3 . When protoxide, or carbonate of manganese, is exposed for some time to a red-heat in an open vessel, it absorbs oxygen, and is converted into a deep-brown powder. An oxide similarly constituted is also obtained by heating the pure peroxide of manganese in a platinum crucible till it ceases to give out oxygen at dull redness. By exposing protonitrate of manganese to a red-heat, the sesquioxide remains as a black powder; and this is perhaps the most certain way of obtaining it. The characters of this oxide, in respect to solvents, differ with its state of aggregation; such of its acid solutions which are at first red, become colorless when heated, or when exposed to air and light, and deposit peroxide, while a portion of protoxide remains in solution. They are rendered colorless by sulphuretted hydrogen, by sulphurous acid, and some other deoxidizers. Heated with hydrochloric acid, chlorine is evolved, and with sulphuric acid, oxygen; and a protochloride and protosulphate of manganese result. Digested with nitric acid, a protonitrate and peroxide of manganese are formed. "From the proportion of oxygen and manganese in this oxide, it has sometimes been regarded as a compound of 1 equivalent of peroxide and 1 of protoxide: in that case, it would be constituted like a salt, and should have the properties of that class of compounds; but Mitscherlich has succeeded in combining it with sulphuric acid, and has obtained with it an alum similar in form and constitution to those of peroxide of iron and alumina; it must therefore be considered as a direct compound of 2 equivalents of manganese and 3 of oxygen." (TURNER.) As a base, therefore it is isomorphous with sesquioxide of iron (Fe_2O_3), and of chromium (Cr_2O_3), and with alumina (Al_2O_3). It gives a violet, or, in small quantity, a pink tinge, to glass, and appears to be the coloring principle of amethyst. It constitutes the mineral called *braunite*, which occurs in octohedral crystals, sp. gr. 4.82. The composition of this oxide is

						Arfwedson and	
						Forchhammer.	Berzelius.
Manganese	2	56	70 70.4 72.74
Oxygen	3	24	30 29.6 27.26
<hr/>						<hr/>	
Sesquioxide of manganese	1		80		100	100.0	100.00

HYDRATED SESQUIOXIDE OF MANGANESE, $Mn_2O_3 + HO$, is obtained by exposing the hydrated and moist protoxide to the action of air, or by passing chlorine through water holding protocarbonate of manganese in suspension, and leaving excess of the latter; for if the chlorine be in

excess, hydrated binoxide is formed. It is a common natural product (the *manganite* of mineralogists), occurring crystallized in rhombic prisms, and massive, sp. gr. 4·3, and so closely resembling the peroxide, that it is often difficult to distinguish them; the powder of the hydrated sesquioxide is, however, generally *brown*, that of the peroxide *black*; the former, heated in a tube, gives off water and little oxygen; the latter, little moisture and much oxygen. Heated by the blow-pipe with glass of borax, the sesquioxide of manganese dissolves with a red or violet color in the outer flame; in the inner flame it becomes colorless in consequence of deoxidizement, but reacquires color when transferred to the outer oxidizing flame. This hydrate consists of

					Turner.
					<i>Manganite.</i>
Manganese	2	...	56	...	62·92
Oxygen	3	...	24	...	26·97
Water	1	...	9	...	10·11
					89·9
					10·1
Hydrate of sesquioxide of manganese } (manganite)					1
					89
					100·00
					100·0

BINOXIDE OF MANGANESE. PEROXIDE OF MANGANESE. MnO_2 . This is the oxide which most commonly occurs *native*, and is resorted to as the source of the other combinations of this metal. In this country it is common in Devonshire, Somersetshire, and Aberdeenshire. It is found in a variety of forms: compact and massive, pulverulent and crystallized. Many of the latter varieties have a grey metallic lustre, and are found acicularly radiated, and in rhomboidal prisms. Its specific gravity varies between 4·8 and 4·9. It is the *pyrolusite** of some mineralogists. The following analyses of five samples of native peroxide of manganese are given upon the authorities of Berthier (1. 2. 3.), Klaproth (4.), and Turner (5).

	I.	II.	III.	IV.	V.
Peroxide of manganese	93·8	84·0	72·7	99·5	97·8
Peroxide of iron.....	1·0	2·0	1·0	0·0	0·0
Oxide of copper	trace.	trace.	trace.	0·0	0·0
Carbonate of lime	0·0	9·0	24·0	0·0	0·0
Silica	4·0	4·0	1·2	0·0	0·5
Baryta.....	0·0	0·0	0·0	0·0	0·5
Water.....	1·2	1·0	1·1	0·5	1·2
					100·0
					100·0
					100·0
					100·0
					100·0

Under the name of *manganese*, this substance is met with in commerce, and is largely consumed in the manufacture of bleaching compounds. In the laboratory, it is resorted to as a source of oxygen gas, $2MnO_2=Mn_2O_3+O$, for which purpose it should be well dried previous to introducing it into the retort (p. 270): sometimes it is mixed with carbonaceous matter, and then yields carbonic acid: it also generally gives off a little nitrogen upon the first application of heat, the source of which is not obvious. Carbonate of lime, silica, oxide of iron, and some other substances, are, as the above analyses indicate, not unfrequently

* *πύρ* fire, and *λύειν* to set free, or loosen: from the facility with which part of its oxygen is extricated by heat: or, according to Graham, from *πύρ* and *λούειν* to wash, from its use in discharging the color of glass.

associated with it. In the arts it is used to give a black color to earthenware, and to remove the green color which glass derives from protoxide of iron; for this purpose it is added in such quantity only as to peroxidize the iron, by becoming itself protoxide, and neither the peroxide of iron nor the protoxide of manganese, which remain, materially interfere with the color of the glass: in this case, MnO_2 , acting on 2FeO , produces MnO and Fe_2O_3 . A little excess of oxide of manganese is apt to give the glass a pink tint, which as is sometimes seen in plate glass windows, does not appear till after long exposure to light. This oxide is also said to sweeten foul water, or to prevent its becoming putrid. It usually loses weight (water), on being dried at a temperature not exceeding 300° ; at a red-heat it becomes *sesquioxide*; and, intensely heated in an iron tube, or with a minute quantity of carbonaceous matter, part of it becomes *protoxide*. It is not altered by air or water. It is a good conductor of electricity. It forms no combinations with the acids; but such of them as appear to dissolve it, reduce it to the state of protoxide. Gently heated with hydrochloric acid, chlorine is liberated, in consequence of the decomposition of the acid by the oxygen of the oxide (p. 275). $\text{MnO}_2 + 2\text{HCl} = \text{MnCl} + 2\text{HO} + \text{Cl}$. Boiled with sulphuric acid, oxygen is evolved, and a soluble *sulphate of the protoxide* is formed, $[\text{MnO}_2 + \text{SO}_3 = \text{MnO}, \text{SO}_3 + \text{O}]$, together with a small portion of *manganic acid*, (which gives the solution a pink color and bleaching properties?) Nitric acid does not attack it unless it contains sesquioxide, or some deoxidizing agent be at the same time present. Many vegetable acids decompose it by the aid of heat. It consists of

						Berzelius and	
						Forchhammer.	Arfwedson.
Manganese	1	...	28	...	63·6	63·75	64·02
Oxygen	2	...	16	...	36·4	36·35	35·98
<hr/>							
Peroxide of manganese	1		44		100·0	100·00	100·00

As binoxide of manganese is extensively used by the bleacher, and as it occurs of various degrees of purity in commerce, a ready mode of determining its value, or, in other words, the quantity of oxygen *per cent.*, which it contains, is desirable: this may be effected in various ways, but it is generally attained by ascertaining its power of decomposing hydrochloric acid and evolving chlorine: to this end the oxide to be tested is mixed with hydrochloric acid, and heated, and the evolved chlorine is received into a jar containing lime diffused through water, by which a chloride of lime is formed; the quantity of chlorine is then determined by the process already described at p. 639. Other modes of testing this oxide have been suggested. (See KANE's *Elem. Ch.*, 580. GRAHAM, 536. LEVOL, *Chem. Gaz.*, April, 1843.)

Pure peroxide of manganese is sometimes useful as a test of the presence of iodine, bromine, and chlorine: when mixed with a salt containing iodine, and the mixture heated with a little sulphuric acid, the violet vapor of iodine is evolved; the salts of bromine give in the same way a brown vapor; and from the chlorides chlorine is evolved.

HYDRATED PEROXIDE OF MANGANESE is obtained, according to Berthier, by passing excess of chlorine through the protocarbonate of manganese diffused in water; a black powder falls, which, when washed and

carefully dried, consists of 88 peroxide and 12 water. A hydrated peroxide (consisting of 1 atom of peroxide and 1 of water) is formed by precipitating protochloride of manganese by chloride of lime. The soft black mineral known to our miners under the name of *Wad*, is also a hydrate of the peroxide of manganese: it contains 2 atoms of water. Dr. Thomson states that when a neutral solution of protoxide of manganese is mixed with a solution of chloride of soda, made by adding carbonate of soda to a solution of neutral chloride of lime till the lime is all precipitated, a beautiful black precipitate falls, which, when washed and dried, consists of 3 atoms of binoxide and 1 of water.

The mineral called *Psylomelan*, or *black hæmatite*, which has a stalactitic form, is perhaps $\text{MnO}, 2\text{MnO}_2$, but the MnO is sometimes replaced by BaO , CaO , KO , CuO , &c. (GMELIN.) Four hydrates of peroxide of manganese are enumerated by Gmelin, constituted as follows: 1. $4\text{MnO}_2, \text{HO}$. 2. $3\text{MnO}_2, \text{HO}$. 3. $2\text{MnO}_2, \text{HO}$. 4. MnO_2, HO .

RED OXIDE OF MANGANESE. Mn_3O_4 . This is the *oxidum manganoso-manganicum* of Berzelius and Arfwedson: it exists native, constituting the mineral termed *Hausmannite*, which occurs in the form of acute octohedrons, sp. gr. 4.72. The artificial production of this oxide has not been very clearly described: it is said to be formed when the hydrated protocarbonate of manganese, after having been dried in the air, is exposed to a red heat. Arfwedson considers it as a definite monoatomic compound of protoxide and sesquioxide $= \text{MnO}, \text{Mn}_2\text{O}_3$; by others it is represented as $2\text{MnO}, \text{MnO}_2$. According to Regnault, this oxide is formed, with the evolution of hydrogen, when steam is passed over protoxide of manganese at a red-heat; and Turner says it is obtained "by exposing peroxide or sesquioxide to a white-heat, either in close or open vessels."

VARVICITE. A peculiar oxide of manganese was discovered by Mr. R. Phillips among some manganese ores from Hartshill, in Warwickshire, to which, from its locality, he gave the above name. Professor Turner afterwards detected it in the manganese of Ilefeld, in the Hartz. It is harder, and has more lustre, and a more decidedly lamellated texture than the common peroxide: its density is 4.531. It has not been found regularly crystallized, but some of the Hartz specimens yield it in pseudocrystals, having the form of six-sided pyramids of calcareous spar. When strongly heated, it is converted into red oxide, losing 5.725 per cent. of water, and 7.385 of oxygen. It is stated to contain 4 atoms of manganese and 7 of oxygen, or 1 atom of the sesquioxide and 1 of the peroxide.

Manganese.....	4	112	or	Sesquioxide	1	80
Oxygen	7	56		Peroxide	2	88
	<hr/>		<hr/>			<hr/>		<hr/>
	1		168			1		168

In Varvicite 1 atom of this oxide $= 168$, is combined with 1 of water $= 9$, giving for the mineral the equivalent $168 + 9 = 177$. (*Phil. Mag. and Ann.*, v. vi. and vii.)

MANGANIC ACID. MANGANESIC ACID. MnO_3 . When peroxide of manganese is heated to redness with nitrate of potassa, a compound is

obtained, which, when put into water, furnishes a solution exhibiting various tints of green, purple, and red, and which was therefore called *Chameleon mineral*. A similar compound is more perfectly obtained by fusing the peroxide with caustic potassa at a red heat, which furnishes a green substance when the alkali is in excess. With water it affords a deep green solution of manganate of potassa, which is permanent with excess of alkali, but otherwise becomes blue, purple, and ultimately red on exposure to air, in consequence of the formation of permanganate of potassa, by the absorption of oxygen; at the same time it deposits a brown powder, which is hydrated peroxide of manganese, and free alkali is separated. $3[\text{KO}, \text{MnO}_3] = \text{KO}, \text{Mn}_2\text{O}_7 + \text{MnO}_2 + 2\text{KO}.$ Manganic acid has not been isolated, or obtained in the state of hydrate, for when set free from the base it is resolved into hydrated peroxide and oxygen.

According to Mitscherlich manganic and sulphuric acids are isomorphous, and the manganates are isomorphous with the sulphates and also with the chromates. The elements of manganic acid are

					Unverdorben. Frommherz. Mitscherlich.						
Manganese	1	28	53.8	58.74	59.45	54
Oxygen	3	24	46.2	41.26	40.55	46
<hr/>					<hr/>					<hr/>	
Manganic acid	1		52		100.0		100.00		100.00		100

MANGANATE OF POTASSA. The following process is given by Dr. Gregory for the preparation of this salt. Mix 4 parts of finely-powdered peroxide of manganese with $3\frac{1}{2}$ of chlorate of potassa, and add them to 5 parts of hydrate of potassa dissolved in a small quantity of water. The mixture is evaporated to dryness, powdered, and then ignited in a platinum crucible, but not fused, at a low red-heat. Digested in a small quantity of cold water, this affords a deep green solution of the alkaline manganate, which may be obtained in crystals of the same color by evaporating the solution over sulphuric acid in the air-pump. (GRAHAM, (*Elem. of Chem.*, 537.)

PERMANGANIC ACID. HYPERMANGANIC ACID. Mn_2O_7 . This acid has been isolated as a *hydrate* as follows: 1. A *manganate of baryta* is first formed by heating nitrate of baryta with peroxide of manganese to redness: reduce the resulting green compound to fine powder, mix it with water, and add a little dilute sulphuric acid, by which a red solution of *permanganate of baryta* is obtained: concentrate this by evaporation, and carefully decompose it by sulphuric acid: decant the supernatant solution of permanganic acid. (MITSCHERLICH.) 2. Pass carbonic acid gas through finely-powdered manganate of baryta diffused in 30 parts of water, till the green color of the powder becomes brown; decant the deep violet liquor from the residue (which is chiefly carbonate of baryta and hydrate of peroxide of manganese), boil it for fifteen minutes to get rid of carbonic acid and throw down carbonate of baryta, and add a few drops of dilute sulphuric acid to precipitate a little residuary baryta; then decant the clear liquor and evaporate it to one-fourth its bulk, pour it off the deposited hydrate of manganese, and after gentle evaporation, carmine-red acicular crystals of *hydrated permanganic acid* are obtained. (FROMMHERZ.) [Wöhler and Mitscherlich regard the crystals as acid permanganate of baryta, which however does not seem probable if prepared

as directed.] 3. Precipitate the green solution of manganate of potassa by nitrate of lead, wash the precipitate and decompose it by long digestion in a mixture of 1 part of oil of vitriol, and 10 of water. In all cases of the preparation of permanganic acid, the contact of organic matter must be cautiously shunned, for it almost immediately decomposes it, and hence paper filters are inadmissible: this is probably the cause of the discrepancies in the accounts of the permanence of this acid, and the effect of heat and light upon it, and which Berzelius seems inclined to refer to isomeric modification.

The aqueous solution of permanganic acid is of a splendid carmine color, or, by transmitted light, dark violet: its taste is austere and bitterish: it tinges the skin brown, and gives the same tint to litmus and turmeric paper, depositing hydrated peroxide: it is soon decomposed at a boiling heat, and by the greater number of combustible bodies at common temperatures. Its salts, which are of a fine red or purple hue, are more permanent than the hydrated acid: they deflagrate with combustibles: they are all soluble in water, and many of them deliquescent. The permanganates of potassa and soda are obtained from the manganates of those bases, which in aqueous solution pass spontaneously into permanganates: others are formed by saturating the aqueous acid with such bases as have no tendency to higher oxidizement; or, according to Mitscherlich, by mixing chlorides with permanganate of silver and decanting the solution off the resulting chloride of silver. Permanganate of silver, which is the least soluble of these salts, is obtained by adding nitrate of silver to a concentrated solution of another permanganate: it is thrown down partly crystalline. The permanganates in solution are deprived of color and decomposed by ammonia, by sulphurous and phosphorous acids, and by sulphuretted hydrogen. There is an obvious analogy in composition between permanganic and perchloric acids, and the permanganate and perchlorate of potassa are stated by Mitscherlich to be isomorphous.

Permanganic acid, as it exists in combination with bases, consists of

						Forchhammer.
Manganese	2	56	50 43.1
Oxygen	7	56	50 56.9
<hr/>						
Anhydrous permanganic acid.....	1		112		100	100.0

PROTOCHLORIDE OF MANGANESE. MnCl . 1. When peroxide of manganese is heated with hydrochlorate of ammonia, as above directed (p. 698), a solution of *chloride of manganese* is easily obtained from the residue, which, if evaporated by a gentle heat, furnishes transparent pinkish crystals of hydrated chloride. 2. The same salt is obtained by dissolving carbonate of manganese in dilute hydrochloric acid and evaporating the solution. 3. When peroxide of manganese is boiled in hydrochloric acid, as in the common process for evolving chlorine, a solution of chloride of manganese more or less contaminated by iron is obtained, from which a pure chloride may be procured by boiling it down to expel excess of acid, diluting it with water and again boiling with the addition of carbonate of manganese, by which the whole of the peroxide of iron is precipitated. If about one-fourth of the impure solution of chloride of manganese be reserved, and precipitated by carbonate of soda, a quantity of carbonate of manganese will be obtained sufficient to preci-

pitate the iron from the other three-fourths of the liquid, and which may be used for that purpose after it has been washed. The absence of iron in the solution is ascertained by its yielding a white precipitate without any shade of blue, by ferrocyanide of potassium; it may then be evaporated, and the chloride of manganese crystallized in its hydrated form. (EVERITT.) Exposed, out of the contact of air, to a heat gradually raised to redness, the crystals of the hydrated chloride lose water, to the amount of about 40 *per cent.*, and leave a lamellar *anhydrous chloride of manganese*; heated in the contact of air, this chloride is decomposed and converted into an oxide, as is the case with the corresponding chloride of magnesium, so that it must be rendered anhydrous by heating it in a retort, or in a tube through which a current of dry hydrochloric acid gas is transmitted.

The anhydrous chloride, which in its fused state much resembles the corresponding chloride of magnesium, combines, according to Brandes, with 4 equivalents of water, to form the hydrated crystals; it loses 3 of these and retains 1 when dried at 212° , and at a red-heat this last equivalent escapes. 100 parts of water dissolve 38.3 of the anhydrous chloride at the temperature of 50° , 46.2 parts at 88° , and 55 parts at 144° . A higher temperature, instead of increasing, diminishes its solubility. (BRANDES.) Absolute alcohol dissolves half its weight of the anhydrous chloride of manganese, and affords, by evaporation in vacuo, a crystalline *alcoate* containing 2 equivalents of alcohol. (GRAHAM.) It is insoluble in ether and in oil of turpentine. The anhydrous chloride consists of

						J. Davy.	Arfwedson.		
Manganese	1	...	28	...	43·7	...	46	...	44·25
Chlorine	1	...	36	...	56·3	...	54	...	55·75
<hr/>									
Chloride of manganese	1		64		100·0		100		100·00

SESQUICHLORIDE OF MANGANESE, Mn_2Cl_3 , is formed when the sesquioxide is dissolved at a low temperature in hydrochloric acid; a dark brown solution is obtained which, by a slight elevation of temperature, evolves chlorine. (FORCHAMMER.)

PERCHLORIDE OF MANGANESE. Mn_2Cl_7 , has been described by Dumas. It is formed by adding fused chloride of sodium to a sulphuric solution of permanganic acid; the compound passes off in the form of a green vapor, condensable at 0° into an olive-colored liquid. If the vapor be conveyed into a moistened flask, it acquires a red tint, and hydrochloric and permanganic acids are generated. The simplest process for preparing it consists in forming a green chameleon-mineral by fusing peroxide of manganese with potassa, and pouring dilute sulphuric acid upon it, by which a permanganate and sulphate of potassa are obtained on evaporation. By the affusion of strong sulphuric acid these salts yield a solution of permanganic acid, to which small pieces of fused common salt are added, as long as green vapor is evolved. (*Ann. Ch. et Ph.*, xxxvi. 81, and *Edin. Journ. of Science*, viii. 179.) From the phenomena of its formation and decomposition, this chloride is supposed to consist of 2 atoms of manganese and 7 of chlorine: it corresponds, therefore, to the permanganic acid.

AMMONIO-CHLORIDE OF MANGANESE, $\text{MnCl}, \text{NH}_4\text{Cl}$, is a soluble and crystallizable salt, not decomposed by excess of ammonia. It may be formed by adding ammonia to an acid solution of protoxide of manganese, or by mixing a solution of sal-ammoniac and chloride of manganese. When ammonia is added to the solution of chloride of manganese, half of the metal is thrown down in the state of hydrated protoxide, and the remainder forms the double salt. When recently precipitated hydrated protoxide of manganese is digested in solution of sal-ammoniac, the double chloride is formed, and ammonia evolved.

CHLORATE OF MANGANESE, MnO, ClO_5 , formed by decomposing chlorate of baryta by protosulphate of manganese, when concentrated to a certain degree by evaporation over sulphuric acid, is decomposed into chlorine, oxygen, and hydrated peroxide of manganese; but the dilute solution is not altered even on boiling. The addition of dilute sulphuric acid renders it intensely red by the formation of persulphate of manganese (permanganic acid?) at the expense of the oxygen of the chloric acid. Added to excess of sulphuric acid, a brown crystalline precipitate falls, consisting of peroxide and protosulphate of manganese. (WAECHTER.)

IODIDE OF MANGANESE, MnI , as formed by the action of hydriodic acid on protoxide of manganese, is a very soluble colorless compound, yielding on evaporation a crystalline mass, fusible without decomposition, when air is excluded, but when heated in the air evolving iodine and leaving protoxide. (LASSAIGNE.)

						Lassaigne.
Manganese	1	28	18.18 17.62
Iodine	1	126	81.82 82.38
<hr/>						<hr/>
Iodide of manganese	1		154		100.00	100.00

IODATE OF MANGANESE, MnO, IO_5 , is thrown down as a pale red crystalline powder on mixing hot concentrated solutions of protacetate of manganese and iodate of soda: it is soluble in about 200 of water. (RAMMELSBERG.)

BROMIDE OF MANGANESE. MnBr . A pale red fusible compound, obtained by heating manganese in bromine vapor, or by evaporating a solution of protoxide of manganese in hydrobromic acid and heating the residue out of the contact of air: heated in the air it evolves bromine and leaves oxide: it is very deliquescent and yields acicular hydrated crystals when its aqueous solution is evaporated. (LÖWIG. BERTHEMOT. *Ann. Ch. et Ph.*, XLIV. 392.)

BROMATE OF MANGANESE. MnO, BrO_5 . Protocarbonate of manganese dissolved in aqueous bromic acid presently decomposes into bromine and hydrated peroxide. (RAMMELSBERG, *Poggend.*, LV. 66.)

FLUORIDE OF MANGANESE. MnF . Protocarbonate of manganese dissolved in aqueous hydrofluoric acid, yields small amethystine crystals, not decomposed by a red heat and soluble in excess of acid. *Sesquifluoride of manganese*, Mn_2F_3 , formed by dissolving hydrated sesquioxide in

hydrofluoric acid, gives dark reddish-brown crystals, soluble in water, but when much diluted depositing a basic salt, an acid salt remaining in solution. (BERZELIUS.)

PERFLUORIDE OF MANGANESE. Mn_2F_7 . By mixing the green chameleon-mineral with half its weight of pure fluor-spar in fine powder, and decomposing the mixture in a platinum vessel by anhydrous sulphuric acid, a vapor, of a deeper tint than chlorine, is evolved, which acquires a red color on mixture with atmospheric air, and gives with water a red solution of hydrofluoric and permanganic acids. It is decomposed by the contact of glass, fluosilicic acid is formed, and a brown powder deposited, which gives a red solution with water. (WÖHLER. DUMAS. *Edin. Journ. of Science*, ix. *Ann. Ch. et Ph.*, xxxvi. 82.)

NITRATE OF MANGANESE. MnO,NO_5 . Dilute nitric acid dissolves moist protoxide or protocarbonate of manganese, and forms a *protonitrate*, which may be obtained by evaporation in vacuo, in prismatic crystals, deliquescent, very soluble in water and in alcohol, and of a bitter taste; their alcoholic solution burns with a green flame. The same salt may be obtained by digesting peroxide of manganese in nitric acid with a portion of gum or sugar, which abstracts oxygen, carbonic acid is evolved, and the protoxide dissolved by the acid. Exposed to light, the solution of the protonitrate lets fall a portion of peroxide of manganese. When dilute nitric acid is poured upon the deutoxide of manganese, a protonitrate and peroxide are formed. According to Millon the crystals are $MnO,NO_5, 6HO$: according to Thomson they consist of

Protoxide of manganese.....	1	...	36	...	23·5
Nitric acid	1	...	54	...	35·3
Water	7	...	63	...	41·2
<hr/>					
Crystallized protonitrate of manganese.....	1		153		100·0

SULPHURET OF MANGANESE. MnS . When dried protosulphate of manganese is ignited with one-sixth its weight of finely-powdered charcoal, or when a current of sulphuretted hydrogen is passed over the protocarbonate or protosulphate heated to redness, a true *sulphuret of manganese* is obtained. (BERTHIER, *Ann. Ch. et Ph.*, xxiv. 273. ARFWEDSON, *Ann. of Phil.*, vii. 332.) It has a grey metallic lustre, and is perfectly soluble in dilute sulphuric and hydrochloric acid, with the evolution of sulphuretted hydrogen gas. It is identical with the *native sulphuret of manganese*, a rare ore, found in Cornwall and Transylvania. Sulphuret of manganese consists of

					Döbereiner.	Arfwedson.			
						<i>Artificial.</i>	<i>Native.</i>		
Manganese	1	...	28	...	63·6	...	63·13	...	62·58
Sulphur	1	...	16	...	36·4	...	36·87	...	37·42
<hr/>									
Sulphuret of manganese	1		44		100·0		100·00		100·00

When sulphur is heated with peroxide of manganese, sulphurous acid is evolved, and a greenish substance obtained, which is probably a sulphuretted oxide. When hydrogen is passed over protosulphate of manganese at a red heat an *oxysulphuret* is also produced = MnO,MnS . (ARFWEDSON.)

When a solution of protosulphate of manganese is mixed with a solution of carburet of sulphur in caustic potassa, a grey precipitate falls, which, when stirred so as to bring it to the surface, assumes a fine purple color: this tint gradually disappears, and it assumes the color of the precipitated sulphuret of manganese. (BERZELIUS.)

Hydrosulphuret of Manganese, MnS, HO , or MnO, HS , is the white or pale-red flocculent precipitate which falls on adding an alkaline hydrosulphuret to solution of a protosalt of manganese: when washed and dried, it acquires a brown color, and if heated in a retort yields water and sulphuret of manganese.

HYPOSULPHITE (DITHIONITE) OF MANGANESE. $\text{MnO}, \text{S}_2\text{O}_2$. This salt has only been obtained in solution, for when protosulphate of manganese is decomposed by hyposulphite of baryta, the filtered solution rapidly decomposes into sulphur and sulphate of manganese, even when evaporated in vacuo over oil of vitriol. (RAMMELSBURG, *Poggend.*, lvi. 305.)

SULPHITE OF MANGANESE. MnO, SO_2 , is obtained by passing sulphurous acid through a mixture of carbonate of manganese and water till the carbonic acid is expelled. It is a white granular tasteless powder, insoluble, or nearly so, in water and in alcohol, and not altered by exposure to air. It dissolves in excess of sulphurous acid, and is decomposed by heat. (BERTHIER.) Its formula is $\text{MnO}, \text{SO}_2, 2\text{HO}$. (JOHN.)

HYPOSULPHATE (DITHIONATE) OF MANGANESE. $\text{MnO}, \text{S}_2\text{O}_5$. When peroxide of manganese (previously digested in nitric acid and thoroughly washed, to deprive it of hydrated oxide) is diffused through water, and sulphurous acid passed into it, a neutral hyposulphate of the protoxide is obtained. It affords a deliquescent salt on evaporation. (See p. 402.)

SULPHATE OF MANGANESE. MnO, SO_3 , is formed, (1.) by dissolving the protoxide or protocarbonate in dilute sulphuric acid, and evaporating; (2.) by mixing peroxide of manganese into a paste with sulphuric acid, and heating it for some time to dull redness; oxygen is evolved, and the dry mass washed with water affords a solution of the sulphate of the protoxide, which may be crystallized by evaporation. This salt is much used in dyeing and calico-printing, for which purpose it is prepared by "igniting peroxide of manganese mixed with about one-tenth its weight of pounded coal in a gas retort. The protoxide thus formed is dissolved in diluted sulphuric acid with the addition at the end of a little hydrochloric acid; the sulphate is evaporated to dryness, and again heated to redness in the gas retort; the iron is found, after the ignition, in the state of peroxide, and insoluble, the persulphate of iron being decomposed, while the sulphate of manganese is not injured by the temperature of ignition, and remains soluble. The solution is of an amethystine color, and does not readily crystallize. When cloth is passed through sulphate of manganese and afterwards through a caustic alkali, protoxide of manganese is precipitated upon it and rapidly becomes brown in the air; or it is at once peroxidized by passing the cloth through a solution of chloride of lime. The color thus produced is called *manganese brown*." (GRAHAM.)

Sulphate of manganese, as obtained by gentle evaporation from the

neutral solution, forms rhombic prisms which contain 4 atoms of water. When the crystals are formed between 45° and 68° , they contain 5 atoms of water, and are isomorphous with sulphate of copper; and when formed under 42° they include 7 atoms of water, and are isomorphous with sulphate of iron. (MITSCHERLICH.) And lastly, when a concentrated solution of sulphate of manganese is mixed with sulphuric acid, it yields on evaporation small granular crystals containing only 1 atom of water. The solubility of sulphate of manganese varies with its water of crystallization; but, according to Brandes, the anhydrous salt is soluble in 2 parts of water at 60° , and in its own weight at 122° ; at a higher temperature its solubility diminishes. It is insoluble in alcohol. The taste of sulphate of manganese is styptic and bitterish, and the crystals have generally a slight tinge of pink. At 240° , they lose 3 atoms of water, but retain 1 until heated above 400° ; at a red heat the salt becomes anhydrous, and in that state consists of

Protoxide of manganese.....	1	36	47.4
Sulphuric acid.....	1	40	52.6
<hr/>					
Anhydrous protosulphate of manganese	1		76		100.0

SESQUISULPHATE OF MANGANESE. $\text{Mn}_2\text{O}_3 + 3\text{SO}_3$, is formed, according to Kane, by dissolving the sesquioxide in sulphuric acid: the solution is of a crimson color; when heated it gives off oxygen and becomes colorless: it is instantly bleached by sulphurous acid or any deoxidizing agent. "Its most important property is that of forming with sulphate of potassa or of ammonia, double salts crystallizing in octohedrons, which are *manganese alums*, similar in constitution to the ordinary alum, but with Al_2O_3 , replaced by Mn_2O_3 . 1 part of peroxide of manganese mixed with 13 of oil of vitriol, and gently heated till half the quantity of oxygen thus separable has escaped, yields a mass from which water extracts the sesquisulphate; 1 part gives a red color to 1280 of water." (R. PHILLIPS, *Phil. Mag.*, v. 214.)

AMMONIO-SULPHATE OF MANGANESE. $\text{MnO}, \text{NH}_4\text{O}, 2\text{SO}_3, + 6\text{HO}$, is a soluble and crystallizable salt, obtained when sulphate of ammonia and protosulphate of manganese are mixed in atomic proportions. Its crystals contain 7 atoms of water, and are of a pale rose-color. According to H. Rose, 100 parts of anhydrous sulphate of manganese absorb 45.30 of dry ammonia, forming a white bulky powder $= \text{MnO}, \text{SO}_3 + 2\text{NH}_3$: the ammonia escapes by exposure to air or heat.

AMMONIO-SESQUISULPHATE OF MANGANESE. $\text{NH}_4\text{O}, \text{SO}_3 + \text{Mn}_2\text{O}_3, 3\text{SO}_3 + 24\text{HO}$. When the purple solution of sulphate of sesquioxide of manganese obtained by gently heating the peroxide with oil of vitriol is mixed with sulphate of ammonia it affords, (from the acid liquor) red octohedral crystals having the above formula: they are decomposed by water, and deposit oxide of manganese. (MITSCHERLICH.)

POTASSA-SULPHATE OF MANGANESE. $\text{KO}, \text{SO}_3, \text{MnO}, \text{SO}_3 + 6\text{HO}$, forms colorless crystals, containing 6 atoms of water. (BERZELIUS.) According to Mitscherlich the crystals have a flesh-red color, the same shape as

those of the ammonio-sulphate of magnesia, and contain 6 atoms of water.

SODA-SULPHATE OF MANGANESE. $\text{NaO}, \text{SO}_3 : \text{MnO}, \text{SO}_3 : + 5\text{HO}$. When chlorine is prepared from salt, sulphuric acid, and peroxide of manganese, the residue furnishes sulphate of soda, and in the mother-liquor, after a year's exposure in a cool place, Geiger found crystals having the above formula: other crystals were formed, having only 2 atoms of water. (*Geiger's Mag. der Pharm.* See also GMELIN, *Handbuch*.)

PHOSPHURET OF MANGANESE, obtained by dropping phosphorus on red-hot manganese, is of a blue-white metallic lustre, and considerably inflammable: it is permanent in the air, brittle, and easily fused. (PELLETIER, *Ann. de Ch.*, xiii. 137.) Rose obtained this phosphuret by passing phosphuretted hydrogen over heated chloride of manganese.

HYPOPHOSPHITE OF MANGANESE, was obtained by Rose, by boiling hypophosphite of lime with excess of protoxalate of manganese, and evaporating the filtered liquor: it did not crystallize. (*Poggend.*, xii. 87.) Wurtz obtained it in small brilliant crystals, permanent at 212° , but losing an atom of water at 300° . Their formula is $\text{MnO}, \text{PO}, 3\text{HO}$. (*Ann. Ch. et Ph.*, Fevr. 1846.)

PHOSPHITE OF MANGANESE. $2\text{MnO}, \text{PO}_3. + 2\text{HO}$. When an aqueous solution of terchloride of phosphorus neutralised by ammonia is added to protochloride of manganese a red precipitate is obtained, constituted as above. (H. ROSE, *Poggend.*, ix.)

PHOSPHATE OF MANGANESE, is precipitated in the form of a white nearly insoluble powder, by adding phosphate of soda to sulphate of manganese. Berzelius observes, that in analyses this salt is difficultly distinguished from phosphate of lime and phosphate of magnesia. It is, however, decomposed by boiling with caustic potassa, and the oxide assumes a dark color.

Phosphate of Sesquioxide of Manganese is formed by heating the sesquioxide or binoxide with concentrated phosphoric acid nearly to redness: on cooling a violet mass is obtained, which gives a pink solution not decomposed by dilution, and immediately decolorized by sulphuretted hydrogen and by sulphurous acid, and which slowly deposits brownish-red granular crystals. (GMELIN.)

CARBURET OF MANGANESE, is probably always contained in the metal reduced by intense ignition of the oxide with charcoal. The quality of steel is said to be much improved by the presence in it of carburet of manganese, the manufacture of which has been patented by Mr. Heath. The plumbago-like substance called *kish*, occasionally produced in iron-furnaces, is said to consist chiefly of carburet of manganese.

CARBONATE OF MANGANESE, is white (or pale-red), insipid, and insoluble in water. It is precipitated as a hydrate, by alkaline carbonates, from the protochloride or protosulphate: it should be washed with boiled

water, and dried in vacuo over sulphuric acid. When heated it loses water and becomes brown. When the artificial carbonate is carefully dried at 100° it probably consists of

					Ure.		Forchhammer.		Turner.		
Protoxide of manganese	2	...	72	...	57.6	...	57.3	...	51.755	...	56.85
Carbonic acid	2	...	44	...	35.2	...	35.4	...	33.050	...	34.72
Water	1	...	9	...	7.2	...	7.3	...	13.520	...	8.43
	<hr/>			<hr/>			<hr/>			<hr/>	
	1		125		100.0		100.0		98.325		100.00

The *native carbonate* or *spathose manganese*, is an anhydrous monocarbonate, MnO, CO_2 : its crystals are obtuse rhomboids, sp. gr. 3.55, translucent or pearly, and of a red hue: it dissolves slowly in cold hydrochloric acid.

CYANIDE OF MANGANESE falls in the form of a grey insoluble precipitate, when solution of cyanide of potassium is added to a protosalt of manganese. The precipitate is soluble in excess of the precipitant. (BERZELIUS.) When cyanide of manganese is dissolved in cyanide of potassium, the solution yields on evaporation brown acicular crystals which are very easily decomposed. (L. GMELIN.) When protacetate of manganese is mixed with excess of hydrocyanic acid and the mixture neutralised by potassa and evaporated, oxygen is absorbed, the manganous cyanide is converted into manganic cyanide and hydrated manganic oxide, and the manganic cyanide combining with the cyanide of potassium yields as the concentrated solution cools, red crystals, the formula of which is $3\text{KC}_y + \text{Mn}_2\text{C}_y_3$. (MITSCHERLICH.)

SULPHOCYANIDE OF MANGANESE is a colorless soluble salt. It is almost insoluble in absolute alcohol.

BORATE OF MANGANESE is precipitated in the form of a white powder when solution of borate of soda is mixed with protosulphate of manganese. If the salt of manganese be mixed with a salt of magnesia, borax occasions no precipitate, and the borate is itself soluble in sulphate of magnesia. (BERZELIUS.)

CHARACTERS OF THE SALTS OF MANGANESE. The salts of manganese, containing the protoxide, are mostly soluble in water: the solution is colorless or slightly pink, of a bitterish astringent taste, and often becomes turbid and brown by exposure to air. They are not precipitated by sulphuretted hydrogen, by hydriodic acid, or by tincture of galls; they furnish white precipitates with the alkalis, which soon become discolored by exposure to air. The alkaline carbonates throw down white precipitates, which gradually assume a hue of purple; they are precipitated white by ferrocyanide of potassium, and flesh-colored or reddish-brown by hydrosulphuret of ammonia. Ammonia only throws down half the oxide and forms a triple salt with the remainder; or, if there be excess of acid, the triple salt only is formed, and there is no precipitation. Manganese is not thrown down in the metallic state by any of the other metals. When peroxide of lead is heated with dilute nitric acid and a solution of manganese then added, the liquid acquires the purple tint of permanganic acid, which is readily perceptible as the peroxide subsides: by this test very minute traces of manganese may be discovered. (W. CRUM.)

Before the blow-pipe, *oxide of manganese* gives, with microcosmic salt, in the exterior flame, a fine amethyst color, which disappears in the interior flame. With borax it gives a yellowish or reddish glass. Any compound of manganese fused on a platinum wire with carbonate of soda forms green manganate of soda: the addition of a little nitre adds to the delicacy of this characteristic test. When the manganese, from its combination with iron, or any other cause, does not produce a sufficiently intense color in the glass, a little nitre may be added to it while in a state of fusion, and the glass then becomes dark-violet while hot, and reddish-violet when cool.

§ IX. IRON. Fe. 28.

THE most important native combinations of iron, whence the immense supplies for the arts of life are drawn, are the *oxides* and *carbonates*: it is also found combined with sulphur, and with several acids, and is a very common component of a variety of mineral products. It is found in small quantity in some animal and vegetable bodies, and in several mineral waters. The alchymists distinguished it by the name and symbol of Mars, ♂. It has been known from a very remote period, and was employed in the time of Moses for cutting instruments.

Iron is a metal of a grey color, fusible at a white heat, but with great difficulty when it is perfectly pure and free from oxygen, sulphur, and carbon. The actual fusing-point of pure iron has not been accurately determined: it requires the highest heat of a wind-furnace to run down soft iron nails into a button, and therefore, according to Daniell, a temperature equal to about 3300° in the language of Fahrenheit's scale. Its texture varies with the method of working it; in bars or wire it appears longitudinally fibrous, but when it has been long kept at a red-heat it acquires a crystalline texture and has a tendency to cuboidal fracture. Its specific gravity is 7.77 to 7.8. Its specific heat is 0.11379. (REGNAULT.) Upon the same authority the specific heat of cast-steel is 0.11848, and that of cast iron 0.12728. It is the hardest and toughest of the ductile metals: it may be drawn into extremely fine wire, but cannot be hammered out into very thin leaves; it is very tenacious; and at a bright-red or orange-heat it admits of being *welded* or joined by hammering to another piece of the red-hot metal. (This property of *welding* belongs also to platinum and to sodium, but not to other metals.) It is attracted by the magnet, but does not retain magnetism when pure; and at a bright-red heat becomes apparently indifferent to it. (See FARADAY, *Phil. Trans.*, 1846, Part I.) At a very elevated temperature, iron shows symptoms of volatility. When in a very finely divided state, as when reduced from the pulverulent oxide by hydrogen gas at a red-heat, it is said not to conduct electricity; but this is probably an error, although in its ordinary state it stands comparatively low upon the list of the metals arranged in the order of their conducting power. (DAVY. BECQUEREL.) The atomic weight of iron upon the hydrogen scale ranges between 27 and 28. The researches of Berzelius give 27.16; of Stromeyer 27.8; of Gay Lussac 28.3. Turner observes, in reference to these numbers, deduced from the analyses of the *oxides*, "In the uncertainty as to which is the most accurate, I shall continue to use 28, the number gene-

rally adopted in this country." Gmelin adopts 27; Graham 27.18. Referring, however, to the analyses of the oxides, as well as to other compounds, the whole number which most correctly represents the combining weight of iron is 28, which therefore I have retained.

Native Iron. Iron, in a state approaching purity, is found among the grains of platinum from the Uralian mines, and a thin vein of it is said to have been discovered in chlorite slate near Canaan, in the United States of America. The term *native iron* is usually applied to the extraordinary detached masses of the metal which are of meteoric origin. In this state it is flexible, generally more or less cellular, and often contains a green substance of a vitreous appearance, which is a silicate of iron and magnesia (meteoric olivin?) It has been found in Africa and America, and in Siberia, where a mass of it, weighing 1600 lbs., was discovered by Professor Pallas. The mass found in Peru, described by Don Rubin de Celis, weighed 15 tons. In the year 1751, a mass of the same substance was seen to fall from the atmosphere in Croatia, appearing, it is said, as a large globe of fire; it is preserved in the Imperial Museum of Vienna. (See *Nickel*.)

Exposed to heat and air, iron absorbs oxygen, and becomes superficially converted into a fusible oxide; when exposed to damp atmospheric air, it becomes encrusted by a brown substance, called *rust*, which is also an oxide of iron. When iron is in a state of extreme mechanical division its affinity for oxygen is such that it heats and even ignites on exposure to air, and burns into an oxide; this is the case with the metal, as it is obtained by the action of hydrogen upon red-hot oxide of iron, and when thus reduced, at a temperature not sufficient to cause the adhesion of the particles of the metal, and suffered to cool in an atmosphere of hydrogen, it requires the same precautions for its preservation in the metallic state as potassium. In a dense mass, iron is not affected by dry air, and it even retains its polish when immersed in pure distilled water which has been deprived of air by long boiling; but in common water, or in water exposed to air, it soon rusts, more especially where it is in contact both of air and water; and in these cases the change is often very rapid, and depends upon the oxygen which the water takes from the air, and carries in a state of solution to the iron. This oxidizement by water is prevented by the presence of alkalis; and in lime water, or in a weak solution of ammonia, potassa, or soda, the metal keeps its lustre for years; but all acid and most neutral salts appear to have an opposite effect. The cause of this protection is not obvious: it has been ascribed to the absorption by the alkali of carbonic acid, and to the expulsion of the air in water when the alkali is dissolved; but carbonic acid is not necessarily present when iron thus rusts under water, and there is no evidence of the expulsion of the whole of the air by the small quantity of alkali which will prevent rust. By the contact of zinc, iron is protected from all common sources of oxidizement and corrosion. In deep water, according to E. Davy, a black and not a red oxide is formed; and in sea water cast iron is often converted into a substance somewhat resembling plumbago; but these changes generally refer to cast iron or other impure forms of the metal, and are frequently referable to voltaic action.

OXIDES OF IRON. Iron is susceptible of four definite degrees of

oxidizement, forming a *protoxide*, which has not been isolated, but which is the basis of a series of well-defined salts ; a *sesquioxide*, generally termed *red oxide* or *peroxide*; a *black* intermediate oxide, known also under the name of *magnetic oxide*; and a *hyperoxide*, generally called *ferric acid*, but which, like the protoxide, has not been isolated. The formulæ of these compounds of iron and oxygen are as follow :—

1 Protoxide.....	FeO
2 Sesquioxide	Fe ₂ O ₃
3 Black oxide	Fe ₃ O ₄
4 Ferric acid	FeO ₃

PROTOXIDE OF IRON. FERROUS OXIDE. FeO. When a solution of potassa is added to a solution of a pure protosalt of iron, every precaution being taken to exclude the presence of oxygen, a white precipitate falls, which is a *hydrate of protoxide of iron*: it is very difficult to wash and dry it under the entire exclusion of air, but when this is done, it is a pale greenish friable substance, not magnetic, and immediately absorbing oxygen when exposed to air so as to become hot, or even ignited, and converted into peroxide: it rapidly absorbs carbonic acid, and dissolves in the dilute acids. When boiled in water it blackens, being converted into a hydrate of the magnetic oxide (according to Wöhler); or perhaps, if air be always cautiously excluded, into an anhydrous protoxide; but in the presence of any oxygen, it becomes first of a dingy green, and then yellow-brown. These green and brown products are either hydrates of the magnetic and of the peroxide, or different states of hydration of the peroxide. When pure iron is carefully dissolved in dilute sulphuric acid, a sulphate of the protoxide is formed: the iron is oxidized by the decomposition of the water, so that the hydrogen which is evolved becomes the indicator of the quantity of oxygen with which a given weight of iron has combined, and this is at the rate of 1 grain of hydrogen for every 28 of iron which is dissolved, and which, therefore, has combined with 8 of oxygen. Again, we find the composition of the protoxide of iron deduced from the experiments of Berzelius and of Gay Lussac to be 77·78 iron, and 22·22 oxygen *per cent.*; and 22·22 : 77·78 :: 8 : 28·003, so that thus far the number 28 accurately represents the atomic weight of iron upon the hydrogen scale, and the protoxide will therefore consist of

						Döbereiner.	Bucholz.	Berzelius.	Gay Lussac.				
Iron	1	28	77·77	76·9	77	77·62	77·94
Oxygen... ..	1	8	22·23	23·1	23	22·38	22·06
<hr/>													
Protoxide of iron	1		36		100·00		100·0		100		100·00		100·00

The salts of the protoxide of iron (protosalts of iron) when crystallized or hydrated, are mostly greenish-blue, but white, or nearly so, when anhydrous. In aqueous solution they have an inky taste, and are very prone to pass into salts of peroxide. The fixed alkalis throw down their oxide as hydrate, which, at first white or pale green, rapidly becomes dark green and brown by exposure. With ammonia only half the oxide is precipitated, and the residue remains, forming a green solution, which, on exposure, becomes covered with a brown film: this solution is at once formed, if sal-ammoniac be previously added to the solution of the protosalt, and then ammonia occasions no precipitate. Carbonate of potassa

and of soda, and sesquicarbonate of ammonia, throw down a white protocarbonate of iron, which soon becomes brown, and which, if solution of sal-ammoniac be added, is redissolved, forming the solution just mentioned. Bicarbonates of potassa and soda produce the same precipitate, unless the solution be very dilute, in which case the mixture is clear, but deposits protocarbonate of iron if boiled, and exposed to air it gradually lets fall hydrated oxide. Sulphuretted hydrogen does not precipitate the salts of the protoxide of iron with the stronger acids; but the alkaline hydrosulphurets throw down a black protosulphuret of iron, insoluble in the precipitant, but easily soluble in hydrochloric acid. Phosphate and arseniate of soda give white precipitates which become bluish and greenish by air. With ferrocyanide of potassium these salts give a white precipitate if entirely free from peroxide, otherwise pale blue; with sesquiferrocyanide they give Prussian blue even when very dilute. Tincture of galls does not immediately discolor a solution of pure protosalt, but if an alkali be added, or a trace of peroxide present, a purple tint ensues. The solutions of the protosalts of iron absorb nitric oxide gas; those which are insoluble in water are soluble in aqueous hydrochloric acid.

SESQUIOXIDE OF IRON. PEROXIDE OF IRON. FERRIC OXIDE. Fe_2O_3 . When a protosalt of iron is boiled with nitric or nitrohydrochloric acid, it becomes peroxidized, and on adding ammonia, a brown hydrated precipitate falls, which, when washed and ignited, is the sesquioxide. When protosulphate of iron is decomposed by a very high temperature, a red powder remains, which is also the peroxide, and which was formerly called *colcothar*. It is also formed by deflagrating iron filings with nitre, and washing the residue: this constituted the *Saffron of Mars* (*Crocus Martis*) of ancient pharmacy. The color of the peroxide of iron varies according to the mode of its formation and the temperature to which it has been subjected: it is generally a reddish or yellow-brown powder, which acquires a darkened hue by a moderate red-heat, and is not magnetic. When, however, it has been long and strongly heated, portions of it sometimes become magnetic. It consists of

										Gay					
										Lussac.	Bucholz.				
										Döbereiner.	Berzelius.	Stromeyer.			
Iron.....	2	56	70	69	69·22	69·85	70·27	70·42
Oxygen	3	24	30	31	30·78	30·15	29·73	29·58
<hr/>															
Peroxide of iron	1		80		100		100		100·00		100·00		100·00		100 00

This oxide of iron is a weak base, or what has sometimes been called an *indifferent oxide*: its salts generally have a brown color and an acid reaction, and when very dilute their solutions are decomposed by boiling, in which case the acid of the salt combines with the water and the peroxide is precipitated. In some cases this oxide even acts as an acid. It is thrown down from its solutions by ammonia, potassa, and soda, in the form of a bulky brown or orange *hydrate*, and in that state is easily redissolved by acids; but when it has been well dried and exposed to an intense heat, it becomes intractable, and difficultly acted upon by the greater number of the acids. When dried at 212° , it is $2\text{Fe}_2\text{O}_3 + 3\text{HO}$; at 400° it becomes $\text{Fe}_2\text{O}_3 + \text{HO}$. A temperature exceeding 500° is required to drive off the whole of the water. (YORKE. *Mem. Ch. Soc.*, II. 325.) After long exposure to air, it almost always contains traces of ammonia.

When precipitated by excess of the fixed alkalis or their carbonates, it carries down a portion of the alkali, which cannot be entirely removed by washing, and if the alkali be not in excess, the precipitated oxide is not free from the acid or from a subsalt: hence the necessity of precipitating by excess of *ammonia*, when the resulting hydrated oxide may be deprived by heat, both of water and of excess of the precipitant. When certain organic substances are present in solutions of this oxide, they prevent its precipitation by the alkalis. This is the case with the serum of the blood, and with hot solutions of gelatin, starch, gum arabic, starch sugar and diabetic sugar, glycerine, and mannite. Tartaric, citric, malic, mucic, kinic, and pectic acids, produce the same effect. This oxide of iron is easily reduced by the action of hydrogen at a temperature even below redness. When gently heated with charcoal, it is converted into magnetic oxide, and at a high temperature is reduced.

Phosphate and arseniate of soda give white precipitates even in very dilute solutions of the salts of peroxide of iron: with the alkaline hydro-sulphurets they afford black precipitates, the whole of the iron being thrown down as sulphuret; with succinate and with benzoate of ammonia they give reddish-brown precipitates, provided there be no excess of acid; under the same circumstances they are blackened by tincture of galls even when in a state of extreme dilution. (Excess of acid being removed by ammonia, 1 part of peroxide of iron in 300,000 of water is sensible to this test.) Sulphocyanic acid and the alkaline sulphocyanides give a blood-red tint to the solutions of the persalts of iron which is very characteristic, even when they are largely diluted. Ferrocyanide of potassium is also a most sensible test of their presence, which it indicates by the formation of Prussian blue. All the persalts of iron which are insoluble in water are soluble in or decomposed by hydrochloric acid.

BLACK OXIDE OF IRON. DEUTOXIDE OF IRON. FERROSO-FERRIC OXIDE. Fe_3O_4 ; or $\text{FeO}, \text{Fe}_2\text{O}_3$. The octohedral *magnetic iron ore* appears to be a definite compound of the two oxides as represented by the preceding formula. According to Gay Lussac a similarly constituted oxide is formed by passing the vapor of water over red-hot iron in a porcelain tube. (*Ann. de Chim.*, LXXX., and *Ann. Ch. et Ph.*, i.) The scales of iron obtained from the smith's forge, the oxide formed when iron is burned in oxygen gas (p. 273), and the black powder formed by the action of air on moistened iron filings, and formerly called *Martial Ethiops*, are allied to this deutoxide, but in these the protoxide or peroxide may occasionally predominate, so that they can scarcely be regarded as definite in their composition. Liebig and Wöhler produced this oxide by mixing dry protochloride of iron with excess of carbonate of soda, calcining the mixture in a crucible, and treating the mass with water: the double oxide remained as a black powder, capable of being washed and dried without change: by dissolving this oxide in hydrochloric acid, and precipitating by ammonia they obtained it in the state of *hydrate*; it was attracted by a magnet even when suspended in water. "When ignited and anhydrous, this double oxide is much more magnetic than iron itself." (GRAHAM.)

The following is Mr. Mercer's method of preparing this oxide (T. S. THOMSON. *Mem. Chem. Soc.*, Novr. 1841): "Take a pound of crystal-

lized protosulphate of iron, dissolve it in water, and add nitric acid in sufficient quantity to peroxidize it, and afterwards carefully expel all excess of nitric or nitrous acid, by boiling. To this add one pound of the protosulphate of iron with water sufficient for its solution. Pour the mixture into a solution of caustic potash, sufficient in quantity and strength to decompose the whole. The precipitate thus thrown down consists of a mechanical mixture of the protoxide and peroxide of iron, atom to atom; raise the temperature of the mixture to 212° , and their chemical union is effected. That such is the change is proved by dipping into the mixture, previous to boiling it, a piece of clean cotton cloth, which after exposure to the air for a few minutes, and washing in water, exhibits the buff stain peculiar to peroxide of iron; but after boiling, a dirty black stain is obtained, indicating the formation of a definite oxide." This is further proved, Mr. Thomson adds, by the oxide, after boiling, having a crystalline structure when examined under the microscope, the minute plates having a brown color, and being transparent. He observes that this oxide, either dry or suspended in water, is well adapted from its extreme susceptibility of magnetism, to indicate the direction of magnetic currents, the curve described by Brewster being well exemplified by it.

The composition of the true deutoxide, in reference to Gay Lussac's analysis, is

						Gay Lussac.	Despretz.	Berzelius.
Iron	3	84	72.41 72.5 72.46 71.86
Oxygen	4	32	27.59 27.5 27.54 28.14
<hr/>								
Deutoxide of iron	1		116		100.00	100.0	100.00	100.00

The salts of this oxide are obtained either by oxidizing the protosalts or deoxidizing the persalts, or by mixing the protosalts and persalts, or by the solution of the deutoxide in acids. Like the protosalts, they pass by oxidizement into persalts, and many substances, such as sulphuretted hydrogen, &c., change them by abstraction of oxygen, into protosalts. They may be regarded as mixtures of protosalts and persalts, to one or other of which many of their reactions belong. The dark green or brown, or the black precipitate which they afford with alkalis, and the blue with cyanide of potassium, are their peculiar characters; in common with the protosalts, they give a blue precipitate with ferridcyanide of potassium, and their reactions in respect to meconic acid, tincture of galls, sulphocyanic acid, and ferrocyanide of potassium, are similar to those of the salts of the peroxide.

FERRIC ACID. FeO_3 . This compound was discovered by Fresny during his researches on the metallic acids. (*Comptes Rendus*, Jan. 1841. *Phil. Mag.*, May, 1841.) It has also been described by J. D. Smith, who gives the following as the preferable mode of forming it. (*Chem. Gaz.*, June, 1843.) Pure and finely divided oxide of iron is mixed with four parts of dried nitre, and exposed for about an hour to a full red-heat in a covered crucible: the result is a dark deliquescent reddish-brown porous mass, which should be powdered while warm, and put into a stopped phial: it is *ferrate of potassa*: its solution should be made with ice-cold water: it has an amethystine tinge so deep as to be nearly opaque, and gradually evolves oxygen, and deposits sesquioxide of

iron: this decomposition is perfect at 212° , and the liquid remains colorless: sulphuric and nitric acids evolve oxygen; hydrochloric acid, chlorine; and oxalic acid, carbonic acid and oxygen. Salts of baryta throw down a bulky red precipitate (*ferrate of baryta*.) (Smith has shown the probability of the existence of another acid of iron, containing less oxygen.) Fresny, in a subsequent paper, has given further details respecting the preparation of the *ferrates*. (*Ann. Ch. et Ph.*, Nov. 1844.) Ferric acid consists of

Iron	1	...	28	53·84
Oxygen	3	24	46·16
<hr/>					
Ferric acid.....	1		52		100·00

FERRATE OF BARYTA. BaO, FeO_3 . When a solution of ferrate of potassa is added to a dilute solution of a barytic salt a bulky crimson precipitate falls, which may be washed and dried at 212° . When carefully heated, it loses water and becomes green, but at a higher temperature oxygen is evolved; before drying, it is decomposed by acids, even by carbonic acid, though but slowly by sulphuric acid. The hydrated salt is $\text{BaO}, \text{FeO}_3 + \text{HO}$, or

						D. Smith.
Baryta	1	77	55·79 52·81
Ferric acid	1	52	37·67 40·86
Water	1	9	6·54 6·33
<hr/>						
Hydrated ferrate of baryta	1		138		100·00	100·00

Native Oxides of Iron. These constitute a very extensive and important class of metallic ores. They vary in color, depending upon mere texture in some cases; in others, upon the degree of oxidizement. Some are magnetic, and those which contain least oxygen are attracted by the magnet. From these oxides the commercial demands for iron are largely supplied: an outline of this manufacture will be given at the end of this Section, when the other combinations of the metal have been described. The following are some of the principal mineralogical varieties of the oxides of iron. (1.) *Magnetic iron ore* (*Fer oxidulé*) is generally black, with a slight metallic lustre. It occurs massive and octohedral. It is often powerfully magnetic; its specific gravity is 4·5. It occurs chiefly in primitive countries, and is abundant at Roslagen in Sweden, where it is manufactured into a bar-iron particularly esteemed for making steel. (2.) Another variety of native oxide of iron is called *iron-glance*, *specular*, and *micaceous iron-ore* (*Fer oligiste*.) It is found crystallized of singular beauty, in the Isle of Elba, and occasionally among the volcanic products of Vesuvius and the Lipari Islands. The crystals are derived from a rhomboid. Its specific gravity is 5·0 to 5·2; it yields a reddish powder. (3.) *Hæmatite*, or red iron-stone: it occurs in globular and stalactitic masses, having a fibrous and diverging structure. It is sometimes cut into instruments used for burnishing: its density is 4·8 to 5. It abounds near Ulverstone in Lancashire, and much of our iron-plate and wire is made from it. Sometimes it is of a brown, black, or ochraceous color. This, as well as the iron-glance, is a sesquioxide, and does not affect the magnet. There are also several varieties of *hydrated peroxide of iron*, such as the fibrous brown or black hæmatitê, the lenticular,

granular, and pisiform iron ore (*Fer limoneux*), and varieties of ochre and umber. The granular variety supplies, according to Berthier, the principal iron furnaces of France: its specific gravity is 3.9: its powder is yellowish-brown, and it is more easily soluble in acids than the anhydrous ores: it often passes into the next variety. There are, according to Colonel Yorke, 3 native hydrates of peroxide of iron, namely $\text{Fe}_2\text{O}_3 + \text{HO}$; $2\text{Fe}_2\text{O}_3 + 3\text{HO}$; and a third containing single equivalents of the preceding. (*Mem. Ch. Soc.*, II. 323.) (4.) A fourth variety of oxide of iron is known under the term of *clay iron-stone*, on account of the quantity of argillaceous earth with which it is contaminated. It is found in masses of different shapes and sizes, and sometimes in small rounded nodules like peas. Some of the globular masses are called *ætites*. The iron-ore of the coal formations of Shropshire, South Wales, Staffordshire, and Scotland, (which, though far from the purest ore found in this country, is the principal source of the cast and bar iron in ordinary use,) is chiefly a *carbonate*.

IRON AND CHLORINE. There are two chlorides of iron, corresponding in composition to the protoxide and sesquioxide.

PROTOCHLORIDE OF IRON. FeCl , may be obtained, (1.) By passing dry hydrochloric acid gas over red-hot iron wire or turnings; or (2.) By digesting clean iron filings in hydrochloric acid, in which case, as in the former, hydrogen is set free; or by employing protosulphuret of iron instead of metallic iron, when sulphuretted hydrogen is evolved: in both cases a green solution is obtained, which, evaporated out of the contact of air, leaves a residue which is to be exposed to a red-heat. (3.) By heating a mixture of iron filings and hydrochlorate of ammonia.

Protochloride of iron is of a grey color, and after fusion acquires a foliated crystalline texture; it is volatile at a high red-heat, and may be condensed in pale-grey crystals. When heated with access of air, sesquichloride of iron sublimes, and peroxide of iron remains. $6\text{FeCl} + 3\text{O} = 2[\text{Fe}_2\text{Cl}_3] + \text{Fe}_2\text{O}_3$. When the vapor of water is passed over it at a dull red-heat, hydrochloric acid and hydrogen are evolved, and black magnetic oxide of iron remains in the tube. $3\text{FeCl} + 4\text{HO} = \text{Fe}_3\text{O}_4 + 3\text{HCl} + \text{H}$. (GAY LUSSAC. *Ann. Ch. et Ph.*, xxii. 424.)

Protochloride of iron consists of

						J. Davy.
Iron.....	1	28	43.7 45.57
Chlorine	1	36	56.3 53.43
<hr/>						
Protochloride of iron	1		64		100.0	100.00

Hydrated Protochloride of Iron. Dissolved in water free from air, and evaporated in vacuo, this chloride furnishes a crystallizable hydrate. When a saturated solution of iron in hydrochloric acid is evaporated, air being carefully excluded, it yields blue rhombic crystals which become green in the air, and effloresce in air dried over oil of vitriol, into a white powder. Their formula is $\text{FeCl}, 4\text{HO}$.

				Bonsdorff.
Iron	1	28	} 63.95
Chlorine	1	36	
Water	4	36	
<hr/>				<hr/>
Crystallized quaterhydrated protochloride of iron	1		100	100.00

SESQUICHLORIDE OF IRON. PERCHLORIDE OF IRON. Fe_2Cl_3 . (1.) When fine iron wire is heated in excess of chlorine it burns with a red light, and this compound is formed. (2.) A mixture of equal weights of chloride of calcium and calcined sulphate of iron, heated to redness, affords a sublimate of sesquichloride. Sesquichloride of iron forms brilliant and iridescent brown crystals, volatile at a temperature considerably below redness: they consist of

						J. Davy.
Iron	2	56	34.14 35.1
Chlorine	3	108	65.86 64.9
<hr/>						<hr/>
Sesquichloride of iron	1		164		100.00	100.0

Hydrated Sesquichloride of Iron. Sesquichloride of iron is very deliquescent and rapidly soluble in water, with the evolution of heat; when the solution is evaporated to dryness in the air, hydrochloric acid ultimately passes off, and peroxide of iron remains. A solution of this chloride is obtained by dissolving peroxide of iron in hydrochloric acid; it forms a deep-brown liquid, which, when concentrated to the consistence of a syrup nearly, and then exposed to cold, yields crystals, the form of which varies, according to Mitscherlich, with their respective quantities of water: when they form acicular and radiating tufts, they include about 40 *per cent.* of water, being $\text{Fe}_2\text{Cl}_3, 12\text{HO}$; but when they form larger tabular crystals, they contain about 22 *per cent.* of water, and are $\text{Fe}_2\text{Cl}_3, 5\text{HO}$: these latter are best obtained by placing the former over a surface of oil of vitriol under a bell-glass: they deliquesce into a thick fluid, which gradually passes into a mass of the crystals containing 5 atoms of water. (FRITZSCHE.) When a current of chlorine is passed through a solution of protochloride of iron, or when nitric acid is gradually added to it when heated, it is converted into sesquichloride. If a dilute solution of the protochloride be exposed for some days to the atmosphere in a tall jar, and a few drops of ammonia be then introduced at different depths, by means of a glass tube, the precipitate near the surface will be green; a little lower, blue; still lower, grey; then of a dirty white; and, at the bottom, quite white, provided the solution has not been so long exposed as to have become oxidized throughout. The sesquichloride is soluble in alcohol and in ether; the former solution is the *Tinctura ferri sesquichloridi* of the Pharmacopœia; and when ether is agitated with an aqueous solution of the sesquichloride it acquires a yellow color.

AMMONIO-CHLORIDES OF IRON. Protochloride of iron absorbs ammonia, and forms a bulky white powder, which is resolved by water into hydrochlorate of ammonia and hydrated oxide of iron. (FARADAY.) When iron filings are boiled in a saturated solution of sal-ammoniac, hydrogen and ammonia are evolved, and the liquor deposits green crystals of *hydrated protochloride of iron and ammonia*. (BERZELIUS.) When sesquichloride of iron is exposed to ammonia, it is slowly absorbed, and the compound furnishes a clear red solution with water: it contains about 9 *per cent.* of ammonia, being $[\text{NH}_3, \text{Fe}_2\text{Cl}_3]$. (H. ROSE.) When a mixed solution of sal-ammoniac and sesquichloride of iron is set aside to crystallize, or evaporated in vacuo over oil of vitriol, it furnishes red cubic crystals, which are $= [2\text{NH}_4\text{Cl}, \text{Fe}_2\text{Cl}_3, 2\text{HO}]$. (MITSCHERLICH.) They lose 1 atom of water when dried at 150° , and the other when dried

above 300°. (GRAHAM.) When hydrochlorate of ammonia and sesquioxide of iron are mixed and exposed to heat in a proper subliming vessel, a yellow sublimate is obtained, which is the *ens veneris*, *flores martialis*, and *ferrum ammoniatum* of old pharmacy; the *Ferri ammonio-chloridum* of the present *Pharmacopœia* is made by evaporating a mixed solution of sesquichloride of iron and sal-ammoniac to dryness: it consists of 15 *per cent.* sesquichloride and 85 sal-ammoniac, and when decomposed by an alkali yields about 7 *per cent.* of sesquioxide of iron. (R. PHILLIPS.)

POTASSIO-CHLORIDES OF IRON. When concentrated solutions of chloride of potassium and protochloride of iron are mixed, and gently evaporated, green hydrated crystals of the double salt are formed. (BERZELIUS.) With chloride of potassium and perchloride of iron evaporated in *vacuo* over oil of vitriol, yellow-red crystals are obtained = $[2\text{KCl}, \text{Fe}_2\text{O}_3 + 2\text{HO}.]$ (FRITZSCHE.)

PROTOCHLORATE OF IRON. A colorless solution of this salt is obtained by decomposing protosulphate of iron by chlorate of baryta: it soon loses its neutrality, acquiring a cinnamon color, depositing basic perchlorate of iron, and leaving a deep red solution of perchlorate and perchloride of iron. (WAECHTER.)

PROTOPERCHLORATE OF IRON. The filtrate of the mixed solution of perchlorate of baryta and protosulphate of iron in atomic proportions yields, on evaporation, colorless acicular crystals, which become brown on exposure to air. (SERULLAS, *Ann. Ch. et Ph.*, XLVI. 305.)

PROTIODIDE OF IRON, FeI , is formed by digesting iron turnings or wire with iodine in water, taking care to have excess of metal present: a green solution is obtained, which, by evaporation out of contact of air, leaves a grey fusible protiodide of iron. It is soluble in water and alcohol, but the solution absorbs oxygen, and deposits peroxide of iron, unless metallic iron be present; so that to preserve it unchanged some pieces of clean iron wire should be immersed in it. (SQUIRE.) This change results from the decomposition of water, hydriodic acid and oxide of iron being formed. (R. PHILLIPS, Jun.) By careful evaporation in *vacuo* crystals of a hydrated protiodide of iron, including 5 atoms of water, may be obtained. Protiodide of iron consists of

Iron	1	28	18·2
Iodine	1	126	81·8
<hr/>					
Protiodide of iron	1		154		100·0

PERIODIDE OF IRON has not been examined, or, at least, not satisfactorily described: according to Berzelius, the brown powder which falls on exposing the solution of the protiodide to air, is a *hydrated subperiodide*. According to Squire it is merely peroxide of iron. Dumas says that we obtain a solution of periodide of iron by dissolving hydrated peroxide of iron in hydriodic acid; and that a compound of periodide and peroxide of iron is thrown down when a quantity of potassa insufficient for its total decomposition is added to that solution.

IODATES OF IRON. Iodate of potassa throws down a yellowish precipitate in solution of protosulphate of iron. (PLEISCHL.) This appears to be a protiodate of iron. FeO, IO_5 . When iodic acid or iodate of potassa is added to solution of perchloride of iron, a white precipitate, soluble in excess of the perchloride, falls: it is soluble in 500 parts of cold water.

PROTOBROMIDE OF IRON. FeBr . When bromine vapor is passed over red-hot iron wire, a yellow crystalline fusible bromide is obtained, readily soluble in water. (*Ann. Ch. et Ph.*, xxxiii. 331.) At common temperatures bromine and iron act but feebly on each other; but if iron filings, bromine, and water, be heated together, or if iron be dissolved in hydrobromic acid, a solution of protobromide of iron is obtained. It yields tabular rhombic crystals $= \text{FeBr}, 6\text{HO}$. The components of protobromide of iron are

						Berthemot.
Iron	1	28	26.43 26.04
Bromine	1	78	73.57 73.96
<hr/>						<hr/>
Protobromide of iron	1	'	106		100.00	100.00

When iron is dissolved in excess of aqueous bromine, a brown fusible substance is obtained on evaporation, which, when heated, gives off bromine and a yellow sublimate, and protobromide of iron remains. (LÖWIG.)

BROMATE OF IRON. Freshly precipitated peroxide of iron, dissolved in hydrobromic acid, and evaporated in a water-bath, leaves a brown mass, of which only a small part is soluble in water: the insoluble residue is $= 5\text{Fe}_2\text{O}_3, \text{BrO}_5, + 30\text{HO}$. (RAMMELSBERG, *Poggend.*, LV. 68.)

FLUORIDES OF IRON. When iron is digested in hydrofluoric acid, a solution is obtained, which affords small quadrangular tabular crystals; they are colorless, and difficultly soluble in water. Heated rapidly in the air, this salt is decomposed; but if its water of crystallization be slowly and carefully expelled, it then may be fused into a true *fluoride of iron*. When hydrated peroxide of iron is dissolved in hydrofluoric acid, it forms a colorless solution, which yields flesh-colored crystals, slowly soluble in water. Ammonia throws down a yellow precipitate, which is a subfluoride: a double *fluoride of potassium and iron* is obtained in colorless crystals, when a mixed solution of those fluorides is evaporated. (BERZELIUS.)

NITRURET OF IRON. When ammonia is passed over ignited iron wire, the whole of the hydrogen and much of the nitrogen of the ammonia are disengaged, but a portion of the nitrogen is retained in permanent combination with the iron, varying from 6 or 7 to 10 or 11 *per cent*. The resulting compound is white, brittle, and even friable; it is magnetic, and is more acted on by air and water than iron: it is specifically lighter than iron, its density being about 5. When very strongly heated, it loses its nitrogen, but the iron retains the appearance of the compound: the acids act upon it as upon iron, but disengage a mixture of hydrogen and nitrogen; besides which, ammonia is formed, which remains in combination with the acid. (DESPRETZ, *Ann. Ch. et Ph.*, XLII. 122.)

PROTONITRATE OF IRON. When very dilute nitric acid (specific gravity 1.16) is digested upon iron filings, little gas is evolved, and the liquid assumes an olive-brown color from the nitric oxide which it contains, but exposed to the air it becomes pale-green in consequence of the escape of that gas; the alkalis produce a green precipitate in this solution: it cannot be obtained in crystals by the usual process, and passes into pernitrate by exposure to air. It may, however, be crystallized by evaporation in an exhausted receiver over sulphuric acid; it then forms transparent rhomboidal crystals of a light-green color, composed of 1 atom of protoxide of iron, 1 of nitric acid, and 7 of water. (THOMSON.) When protosulphuret of iron is dissolved in dilute nitric acid sulphuretted hydrogen escapes, and a green solution of protonitrate of iron is obtained, which, when gently heated, speedily becomes brown, in consequence of the formation of peroxide. A protonitrate of iron is also formed when solutions of protosulphate of iron and nitrate of baryta are mixed in atomic proportions. The solution of the neutral protonitrate is decomposed near the boiling temperature, with the evolution of nitric oxide, and the abundant precipitation of the subnitrate of the peroxide. Iron turnings may be dissolved in cold and highly concentrated nitric acid, so as to produce ammonia and protonitrate of iron, without the extrication of gas. $8\text{Fe} + 10\text{NO}_5 + 4\text{HO} = 8[\text{FeO}, \text{NO}_5] + \text{NH}_4\text{O}, \text{NO}_5$.

PERNITRATE OF IRON. Nitric acid, diluted with a little water, (sp. gr. 1.35), acts violently on iron and peroxidizes it, a vast quantity of gas being at the same time generated, which consists of a mixture of nitrous and nitric oxides, and a solution is formed of a reddish-brown color, containing *pernitrate* of iron, and affording a brown precipitate to the alkalis. When this solution is evaporated, a brown deliquescent mass remains, soluble in water and alcohol; it is decomposed at a red-heat, and peroxide of iron remains. If this solution be mixed with excess of carbonate of potassa, the precipitate at first thrown down is redissolved by the alkali, and a deep-brown liquid obtained, called in the Pharmacopœia, *Liquor ferri alkalini*; it has long been known in Germany under the name of "Stahl's alkaline tincture of iron." A *crystallized pernitrate* was obtained by Vauquelin from a solution formed by leaving nitric acid long in contact of black oxide of iron: the crystals, which are square prisms and colorless, deliquesce into a reddish-brown liquid; they consist, according to Thomson, of 2 atoms of peroxide of iron, 3 of nitric acid, and 16 of water.

A *hydrated subpernitrate of iron* falls on boiling the diluted solution of the peroxide in nitric acid, or by adding excess of hydrated peroxide to the concentrated nitric solution; when moist it is brown and gelatinous, and sparingly soluble in pure water.

Passive condition of Iron, in respect to the action of Nitric Acid. In all ordinary cases nitric acid of the specific gravity 1.35 acts powerfully upon iron, but under certain circumstances the metal becomes inert, and may be thrown, as it were, into a passive condition; a circumstance first noticed by Schoenbein. This state of things is brought about, 1. By slightly oxidizing the extremity of an iron wire by holding it in the flame of a spirit lamp, and when cold dipping it gradually into the acid, observing to introduce the oxidized end first. 2. By dipping the end of the wire

into strong nitric acid and washing it in water. 3. By first introducing a platinum wire into the acid, and then the iron wire in contact with it, which contact may, however, afterwards be broken. 4. An iron wire already rendered passive acts as the platinum wire, and renders other wires passive in the same way. 5. By making the iron wire the anelectrode or positive conductor of a voltaic pile, and introducing it into the acid after the insertion of the cathelectrode or negative pole; in this case the iron wire behaves as one of platinum, and gives off oxygen gas. This state is destroyed when the passive iron is made the negative pole, or when it is brought into contact with iron or zinc which at the time is in the act of solution by the acid. This condition of iron, connected apparently with its relations to magnetism or electricity, is not confined to nitric acid, but extends to other agents. (SCHOENBEIN and FARADAY, *Phil. Mag. and Ann.*, vols. ix. and xiv. See also some remarks upon this subject by Graham, *Elem. Chem.*)

AMMONIA AND IRON. Iron is not acted upon by aqueous ammonia, nor does it throw down copper from the ammoniacal solutions of oxides of copper. Ammonia added to the protosalts of iron only throws down part of the oxide, and forms a double salt, which, on exposure to air, gradually deposits peroxide in proportion as the protoxide of the double salt absorbs oxygen.

PROTOSULPHURET OF IRON. FeS . 1. When sulphur is dropped upon red-hot iron wire, or fused with iron filings, a compound is obtained, which, after having been heated to expel excess of sulphur, is perfectly soluble in dilute sulphuric acid, with the evolution of pure sulphuretted hydrogen, and which is a protosulphuret of iron. So also, when a thick plate of wrought iron is heated to bright redness, a hole is made in it by pressing a roll of sulphur upon it, the fused protosulphuret of iron running off. 2. White-hot wrought iron, exposed to a jet of sulphur vapor, burns in it, and runs down into the protosulphuret. 3. It is formed by exposing pure yellow pyrites, or bisulphuret of iron, intimately mixed with an equivalent of pure iron, to a red heat; or, 4, By passing dry hydrogen gas over powdered iron pyrites, heated to redness in a glass or porcelain tube. 5. It is thrown down in a hydrated state on adding hydrosulphuret of ammonia to solution of protosulphate of iron. 6. By the mutual action of iron filings and powdered sulphur made into a paste with water.

Protosulphuret of iron is of a dark-bronze color, and influences the magnet. (As obtained in a pulverulent form by passing hydrogen over red-hot iron pyrites, it is not magnetic. SCHAFFGOTSCH.) It is much more fusible than iron; it loses no sulphur, even at a white-heat, out of contact of air; when pure, it is soluble without residue in dilute acids, with the evolution of sulphuretted hydrogen and the formation of a protosalt of iron. When heated in air or oxygen, sulphurous acid and oxide of iron are formed. Digested in strong nitric or nitrohydrochloric acid, a portion of sulphur is separated, the iron is peroxidized, and sulphuric acid is formed. When the moist hydrated protosulphuret (obtained by precipitating a protosalt of iron by hydrosulphuret of ammonia) is exposed to air, the iron becomes oxidized, and sulphur separates, and more or less

sulphurous and sulphuric acids are often formed with heat enough to produce inflammation. This sulphuret consists of

						Hatchett.	Berzelius.	Proust.			
Iron.....	1	28	63·6	63·5	63	62·5
Sulphur	1	16	36·4	36·5	37	37·5
<hr/>											
Protosulphuret of iron	1		44		100·0		100·0		100		100·0

BISULPHURET OF IRON, FeS_2 , is formed, according to Berzelius, when the protosulphuret is well mixed with half its weight of sulphur, and subjected to a high temperature, which, however, must be below redness: a bulky dark-yellow metallic powder is the result, which is not attracted by the magnet, and insoluble in dilute sulphuric and hydrochloric acid. A similar compound is obtained by passing a current of sulphuretted hydrogen over oxide of iron at a temperature just below redness. If natural crystals of black oxide of iron be subjected to this process, they are converted without change of form into the bisulphuret. By slowly heating an intimate mixture of peroxide of iron, sulphur, and sal-ammoniac, till the latter begins to volatilize, Wöhler obtained small yellow cubes and octohedrons of bisulphuret of iron. Lowe has described a similar artificial production of crystals of pyrites in the clay lining of iron pots used in the manufacture of sal-ammoniac from sulphate of ammonia. We have two interesting cases of the formation of this sulphuret in the humid way: the one described by Hatchett occurring in the Mere of Diss, in Norfolk (*Phil. Trans.*, 1797); the other, by Pepys, (*Geol. Trans.*, I. 399,) taking place in the bones of mice which had fallen into a solution of sulphate of iron. It appears that in these cases the organic matter in a state of decomposition, decomposes the sulphuric acid and the oxide of iron. Bisulphuret of iron consists of

						Hatchett.	Berzelius.	Bucholz.			
Iron.....	1	...	28	...	46·7	...	46·7	...	46·08	...	49
Sulphur	2	...	32	...	53·3	...	53·3	...	53·92	...	51
<hr/>											
Bisulphuret of iron	1		60		100·0		100·0		100·00		100

Native Sulphurets of Iron. Hatchett first showed that *magnetic pyrites* is a protosulphuret of iron, and *common* or *yellow pyrites* a bisulphuret; the results of his analyses of these ores are given in the preceding paragraphs. Common pyrites is found massive, and crystallized in a variety of forms, some derived from a primitive cube, others from a rhombic prism, for it appears to be dimorphous; it often occurs in radiated nodules, which, when rolled amongst the shingles upon the sea-beach, are sometimes called *thunder-bolts*; it is of different shades of brass-yellow; its principal use is in the formation of *sulphate of iron*, or *green vitriol*, for which purpose it is gently roasted and exposed to air and moisture. The cubical bisulphuret is very permanent, but some of the prismatic varieties spontaneously pass into sulphate, and when in large masses generate heat enough to produce ignition: in this way beds of coal have been set on fire in consequence of the absorption of oxygen by their contained pyrites. Pyrites has also been used as a source of sulphur, and as a substitute for sulphur in the production of sulphuric acid. (p. 389.)

SESQUISULPHURET OF IRON. Fe_2S_3 . This compound is formed by

passing sulphuretted hydrogen over sesquioxide of iron at a temperature not exceeding 212° ; or by the action of the same gas upon the hydrated sesquioxide at common temperatures. According to Proust, it may be formed by the action of sulphur on the protosulphuret at a very low red-heat: he states it to be magnetic, which Berzelius denies. It is formed in the humid way by adding neutral persulphate of iron, drop by drop, to a solution of an alkaline hydrosulphuret; it then falls as a black powder, which cannot be dried in the air without change. It corresponds in composition to the sesquioxide, and consists of

						Berzelius.	Proust.	Bucholz.			
Iron	2	...	56	...	53·8	...	52·92	...	52·64	...	52·07
Sulphur.....	3	...	48	...	46·2	...	47·08	...	47·36	...	47·93
<hr/>											
Sesquisulphuret of iron	1		104		100·0		100·00		100·00		100·00

DISULPHURET OF IRON, Fe_2S , is formed, according to Arfwedson, by passing a current of hydrogen gas over anhydrous protosulphate of iron, heated to redness: sulphurous acid, water, and sulphuretted hydrogen, are evolved, and 46.47 *per cent.* of the above compound remains. This is probably a definite compound of 1 atom of iron + 1 atom of protosulphuret of iron = Fe, FeS .

TETRA-SULPHURET OF IRON, Fe_4S , is also described by Arfwedson as a definite sulphuret; he obtained it by passing a current of hydrogen over anhydrous subpersulphate (disulphate of the peroxide) of iron. This and the preceding compound are grey and pulverulent, and they both evolve mixtures of hydrogen and sulphuretted hydrogen when dissolved in dilute sulphuric acid.

HYPOSULPHITE OF PROTOXIDE OF IRON, $\text{FeO}, \text{S}_2\text{O}_2$, is obtained together with sulphite by digesting finely-divided metallic iron in sulphurous acid, $[2\text{Fe} + 3\text{SO}_2 = \text{FeO}, \text{S}_2\text{O}_2 + \text{FeO}, \text{SO}_2]$; a solution is obtained at first brown, but becoming green, and no gas is evolved: when evaporated it leaves a dirty-white viscid mass, and is decomposed by exposure to air. (See *Protosulphite of Iron*.) When sulphuric or hydrochloric acid is added to its solution, sulphurous acid is evolved, and sulphur precipitated. This solution furnishes a perfect protosalt of iron; and by keeping a few filings of iron in it, it may be retained in this state. It gives a white precipitate with ferrocyanide of potassium, and infusion of galls does not immediately discolor its dilute solution.

PROTOSULPHITE OF IRON, FeO, SO_2 , may be obtained by digesting recently precipitated protocarbonate of iron in an aqueous solution of sulphurous acid, from which, when concentrated, alcohol throws down the sulphite. According to Fordos and Gélis, (*Ann. Ch. et Ph.*, Juillet, 1843,) when iron is dissolved in sulphurous acid and the solution evaporated in vacuo, crystals of *hydrated protosulphite of iron* are obtained having the formula $\text{FeO}, \text{SO}_2, 3\text{HO}$, and if the evaporation be continued the liquor which has deposited the sulphite will sometimes yield crystals of hyposulphite, but generally the liquid contains, together with hyposulphite, a *sulphuretted hyposulphate*, which is very unstable, and is decomposed by concentration, into sulphur, sulphurous acid, and sulphate: they attribute this second result to the intervention of air. The persalts of iron exert a curious action on the hyposulphites: if, for

instance, perchloride of iron be added to solution of hyposulphite of soda till the mixture no longer becomes violet, for each equivalent of perchloride of iron, 2 equivalents of hyposulphite are decomposed; the persalt of iron is reduced to a protosalt, and the evolved chlorine reacts on the hyposulphite, in the same way as iodine (see p. 614), chloride of sodium being formed, together with one equivalent of bisulphuretted hyposulphate. $2[\text{NaO}, \text{S}_2\text{O}_2] + \text{Fe}_2\text{Cl}_3 = 2\text{FeCl} + \text{NaCl} + \text{NaO}, \text{S}_4\text{O}_5$.

HYPOSULPHATES OF IRON. *Hyposulphate of protoxide of iron*, is formed by mixing a solution of hyposulphate of baryta with protosulphate of iron: the filtered solution furnishes green prismatic crystals, easily soluble, and containing about 30 *per cent.* of water of crystallization, their formula being, according to Heeren, $\text{FeO}, \text{S}_2\text{O}_5, 5\text{HO}$. When hydrated peroxide of iron is digested in aqueous hyposulphuric acid, a brown compound, insoluble in water and alcohol, very difficultly soluble in hyposulphuric, but very soluble in hydrochloric acid, is formed: according to Heeren, when carefully dried it forms a brittle brown mass $= 8\text{Fe}_2\text{O}_3, \text{S}_2\text{O}_5, 20\text{HO}$.

PROTOSULPHATE OF IRON, FeO, SO_3 , is the *copperas* and *green vitriol* of commerce, and is often prepared by exposing roasted *pyrites* or *bisulphuret of iron* to air and moisture, in which case the salt is impure. It is usually formed for medicinal and chemical purposes, by dissolving iron filings or turnings in dilute sulphuric acid, filtering and evaporating the solution, and setting it aside to crystallize. It is also obtained, free from persulphate, by acting upon *protosulphuret* of iron by dilute sulphuric acid. This salt forms, when pure, bluish-green crystals in the form of oblique rhombic prisms, (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 120,) of a styptic taste, reddening vegetable blues, and including 7 atoms of water; $\text{FeO}, \text{SO}_3, 7\text{HO}$. The specific gravity of the crystallized salt is 1.8; that of the anhydrous sulphate, 2.64. The solubility of 1 part of crystallized sulphate of iron at different temperatures is, according to Brandes and Firnhaber, as follows,

Temperature	50°	59°	75°	92°	115°	140°	183°	194°	212°
Water	1.64	1.43	0.87	0.66	0.44	0.38	0.37	0.27	0.30

The aqueous solution is pale-green, and absorbs nitric oxide gas, acquiring a deep olive-brown color. When thus saturated with nitric oxide it appears to take it up in the proportion of 1 equivalent to 4 of the sulphate: it is again evolved when the liquid is either heated or exposed in a vacuum: an alkali added to this solution throws down a grey precipitate, which is perhaps a compound of nitric oxide and hydrated protoxide of iron; it soon becomes green and yellow, evolving nitric oxide, but no nitrate or nitrite is formed. (PELIGOT, *Ann. Ch. et Ph.*, liv. 17.) This compound communicates a red or purple tint to a large volume of cold sulphuric acid: hence the detection of nitric oxide or acid in sulphuric acid, already mentioned (p. 394). (BUSSY and LECANU, *Journ. de Pharm.*, xi. 341.) When chlorine is passed through an aqueous solution of protosulphate of iron hydrochloric acid is formed, and the iron becomes peroxidized; so that water is decomposed. Protosulphate of iron is insoluble in alcohol and in sulphuric acid, both of which deprive the

crystals of water, and precipitate the salt from its solutions in the form of a white powder.

Exposed to dry air, this salt generally effloresces, and in moist air gradually absorbs oxygen and is partly converted into a persulphate, becoming of a rusty or reddish color, whence the French term, *couperose*, applied to it, corrupted into *copperas*. When heated in close vessels, it fuses in its water of crystallization, and at 238° loses 6 equivalents of water, but retains 1 equivalent till heated above 535°; this may be driven off at a higher temperature, and the salt is then white, pulverulent, and anhydrous: at a higher temperature the anhydrous protosulphate is converted into an anhydrous persulphate, and sulphurous acid is at the same time evolved: $2[\text{FeO},\text{SO}_3] = \text{Fe}_2\text{O}_3,\text{SO}_3 + \text{SO}_2$; and at a high red-heat the persulphate is itself decomposed, and leaves peroxide, while the sulphuric acid partly passes off in an anhydrous state and may be condensed in a refrigerated receiver, and is partly resolved into sulphurous acid and oxygen. The residuary red oxide is of a deep color and was formerly known under the name of *colcothar*, or *caput mortuum vitrioli*. It is in consequence of this decomposition that sulphate of iron is often used as a substitute for sulphuric acid, to separate weaker acids from their bases, at high temperatures. Anhydrous protosulphate of iron consists of

					Berzelius.	Wenzel.
Protoxide of iron	1	36	47.4	47.07	42.17	
Sulphuric acid	1	40	52.6	52.93	57.83	
<hr/>						
Anhydrous protosulphate of iron	1	76	100.0	100.00	100.00	

and the ordinary crystals are composed of

					Berzelius.	Thomson.	Mitscherlich.
Anhydrous protosulphate of iron	1	76	54.7	54.6	55	56.08	
Water	7	63	45.3	45.4	45	43.92	
<hr/>							
Crystallized protosulphate of iron	1	139	100.0	100.0	100	100.00	

When a solution of protosulphate of iron is made to crystallize at a temperature of 176°, it forms right rhombic prisms which include 4 equivalents of water, and correspond with the quaterhydrated sulphate of manganese; and when an acid solution of sulphate of iron is boiled down, a saline crust forms, in which the salt is combined with 3 equivalents of water; lastly, by dissolving the salt in sulphuric acid, crystals may be obtained with 2 equivalents of water. (MITSCHERLICH.)

Native Green Vitriol is frequently found associated with iron pyrites, being produced by its decomposition; it occurs in several of our coal-mines. When exposed to air it suffers the same changes as the artificial salt. A *native persulphate of iron* occurs in white granular masses in Chili, forming beds in some places 20 feet deep. (ROSE, *Poggend.*, xxviii.)

PROTOSULPHATE OF IRON AND AMMONIA. $\text{NH}_4\text{O},\text{FeO},2\text{SO}_3,6\text{HO}$. This salt is isomorphous with the ammonio-sulphate of magnesia. (MITSCHERLICH.) It is obtained by evaporating the mixed solution of its component salts: it is more soluble than protosulphate of iron.

PROTOSULPHATE OF IRON AND POTASSA, $\text{KO},\text{FeO},2\text{SO}_3,6\text{HO}$, is obtained by mixing solutions of equivalents of each of the salts; it is of a

very pale tint of green, and the crystals contain 6 equivalents of water (MITSCHERLICH), 5 (THOMSON.)

PERSULPHATE OF IRON. There are several compounds of peroxide of iron with sulphuric acid. The *tripersulphate* (or *neutral persulphate* as it sometimes is called), $\text{Fe}_2\text{O}_3, 3\text{SO}_3$, is obtained by boiling a solution of the protosulphate with the addition of nitric acid: the liquor is evaporated to drive off the nitric acid, and the residue then consists of a mixture of the above tripersulphate and a subpersulphate: the former is soluble in water, and being poured off and evaporated to the consistence of syrup, is imperfectly and difficultly crystallizable: by further evaporation it yields a brown mass, and ultimately a dingy-white anhydrous salt, which at a red-heat gives off anhydrous sulphuric acid: it is deliquescent, and soluble in alcohol; it is insoluble in sulphuric acid, which precipitates it in the form of a white anhydrous salt from its concentrated aqueous solution: when its dilute aqueous solution is heated it deposits a *tribasic salt*, which, when dried at 212° , is a dark orange-colored powder, insoluble in water but soluble in acids $= 3\text{Fe}_2\text{O}_3, \text{SO}_3, 4\text{HO}$. *Monobasic* and *bibasic persulphates* have been described by Soubeiran (*Ann. Ch. et Ph.*, xliv. 329) and Berzelius (*Lehrbuch*). The *fibroferrite* described by Prideaux (*Phil. Mag.*, xviii. 397), appears essentially to be a *sesquipersulphate* $= 2\text{Fe}_2\text{O}_3, 3\text{SO}_3, 18\text{HO}$; and Maus has noticed a bipersulphate, $\text{Fe}_2\text{O}_3, 2\text{SO}_3$, which remains in solution when the (neutral or) tripersulphate is partly decomposed by carbonate of lime. (*Poggend.*, xi. 77.)

According to Dumas, the protosulphate and persulphate of iron are capable of crystallizing together, and forming a kind of double salt; it often occurs in commerce under the name of green vitriol; it is of a dingy grass-green color, whereas the pure sulphate of the protoxide furnishes hydrated crystals which are of a bright bluish-green. It is this salt which is produced when a solution of the protosulphate is exposed to air till it ceases to form an ochrey deposit of subpersulphate. An intermediate sulphate $= 3[\text{FeO}, \text{SO}_3] + 2\text{Fe}_2\text{O}_3, 3\text{SO}_3$, the crystals of which include 4 atoms of water, is also described by Abich. (*Chem. Gaz.*, April, 1844.)

PERSULPHATES OF IRON AND AMMONIA. A crystallized *terpersulphate of iron and ammonia* $= [\text{NH}_4\text{O}, \text{SO}_3, + \text{Fe}_2\text{O}_3, 3\text{SO}_3, + 24\text{HO},]$ is obtained in octohedral crystals resembling alum, by evaporating a mixed solution of sulphate of ammonia and excess of persulphate of iron. The crystals, if at first brown, may be purified by a second crystallization: they are soluble in 3 parts of water at 60° , and consist, according to Forchammer, (*Ann. Phil.*, v. 406,) of

						Forchammer.
Ammonia.....	1	17	3.52
Peroxide of iron	1	80	16.59 16.470
Sulphuric acid.....	4	160	33.18 34.596
Water	25	225	46.71 43.480
<hr/>						
Crystallized tersulphate of perox- ide of iron and ammonia }	1		482		100.00	

Bipersulphate of Iron and Ammonia. $2[\text{NH}_4\text{O}, \text{SO}_3] + \text{Fe}_2\text{O}_3 + 2\text{SO}_3 + 4\text{HO}$, is formed when ammonia is cautiously added to a solution of persulphate of iron, and the mixture left to spontaneous evaporation till the

precipitate begins to be redissolved; brown six-sided prismatic crystals are deposited, (MAUS, *Poggend.*, xi. 79), composed of

Ammonia.....	2	34	10·36	Maus. 10·36
Peroxide of iron	1	80	24·39	23·75
Sulphuric acid.....	4	160	48·78	49·20
Water	6	54	16·47	16·75
<hr/>							
Crystallized bisulphate of perox- ide of iron and ammonia }	1		328		100·00		100·00

PERSULPHATES OF IRON AND POTASSA. *Terpersulphate of Iron and Potassa.* $\text{KO,SO}_3\text{:Fe}_2\text{O}_3\text{,3SO}_3\text{:24HO}$, is obtained by dissolving 1 equivalent of peroxide of iron, 3 equivalents of oil of vitriol, and 1 of sulphate of potassa, in boiling water; on evaporating the solution and setting it aside in a cold place, octohedral crystals, which in form and taste resemble those of common alum, are gradually deposited: they are colorless, or nearly so, being sometimes of a reddish or violet tint, and soluble in 3 parts of water at 52°. This salt is frequently termed *iron alum*, the alumina of common alum being in it replaced by peroxide of iron, with which it is isomorphous. The proximate constituents of this salt are

Potassa	1	48	9·52	Anthon. 9·2
Peroxide of iron	1	80	15·87	15·1
Sulphuric acid.....	4	160	31·74	32·2
Water	24	216	42·87	43·5
<hr/>							
Crystallized tersulphate of per- oxide of iron and potassa }	1		504		100·00		100·0

Bipersulphate of Iron and Potassa. $2[\text{KO,SO}_3]\text{:Fe}_2\text{O}_3\text{,2SO}_3\text{:6HO}$. When solution of potassa is added to a solution of the preceding salt till it just begins to form an insoluble precipitate, and the liquor left to spontaneous evaporation, tabular hexahedral crystals form, soluble in 6 parts of cold water: the solution soon decomposes into subpersulphate of iron and iron alum. The crystals consist of

Potassa	2	96	24·6	Maus. 23·1	Richter. 22·2
Peroxide of iron	1	80	20·5	20·8	21·5
Sulphuric acid	4	160	41·0	41·7	42·1
Water	6	54	13·9	14·4	14·2
<hr/>									
Crystallized bisulphate of per- oxide of iron and potassa }	1		390		100·0		100·0		100·0

PHOSPHURET OF IRON. Fe_4P , is formed by dropping phosphorus into a crucible containing red-hot iron-wire; it is a brittle grey compound, and sometimes crystallizes in rhomboidal prisms. It acts upon the magnet. (Upon the subject of the magnetic qualities of the sulphuret and phosphuret of iron, see Hatchett's analysis of magnetical pyrites. *Phil. Trans.*, 1804.) It may also be procured by the ignition of a mixture of iron filings, phosphoric acid, and charcoal powder; or of phosphate of iron and charcoal. It is very difficultly soluble in the acids. A small portion of this compound is said to be present in all *cold-short iron*, and is eminently injurious to the quality of iron when it is contained in it to the amount of 1 *per cent*. Steel which does not contain more than 1 part in

1000 of phosphuret of iron is rendered harder, and for some particular purposes improved.

Phosphuret of iron obtained by the above processes, consists of

						Berzelius.	Pelletier.		
Iron	4	...	112	...	77.8	...	76.805	...	80
Phosphorus	1	...	32	...	22.2	...	23.195	...	20
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Phosphuret of iron	1		144		100.0		100.000		100

When phosphuretted hydrogen gas is passed over heated iron pyrites, a compound is formed, containing 43 to 45 *per cent.* of phosphorus, and therefore $=\text{Fe}_3\text{P}_2$. In its formation sulphuretted hydrogen is evolved, so that $3\text{FeS}_2 + 2\text{PH}_3 = \text{Fe}_3\text{P}_2 + 6\text{HS}$. (H. ROSE.) No definite compound of phosphorus and iron in single atomic proportions has been obtained.

HYPOPHOSPHITES OF IRON. Iron dissolves in aqueous hypophosphorous acid, evolving hydrogen, and yields on evaporation pale green crystals of a protosalt of iron. Hydrated peroxide of iron is sparingly soluble in cold hypophosphorous acid, and forms a white salt: at a boiling heat it is resolved into protohypophosphite and perphosphate. (H. ROSE, *Poggend.*, xii. 294.) The crystals are octohedrons $=\text{FeO}, \text{PO}$, 8HO , or according to Wurtz, $\text{FeO}, \text{PH}_2\text{O}_3 + 6\text{HO}$. (*Ann. Ch. et Ph.*, Fevr. 1846.)

PHOSPHITE OF IRON. A solution of protosulphate of iron gives a white precipitate with the aqueous solution of terchloride of phosphorus neutralised by ammonia, which when dried in vacuo becomes greenish, and when heated evolves hydrogen and leaves a subphosphate of the protoxide. The same phosphoric solution gives a white precipitate with ammonio-persulphate of iron, which washed with cold water, and dried in vacuo, is a phosphite of the peroxide: it is soluble in excess of the iron solution. (H. ROSE, *Poggend.*, ix. 35.)

PROTOPHOSPHATE OF IRON. $2\text{FeO}, \text{HO}, \text{PO}_5$, is insoluble, and may be formed by adding solution of common phosphate of soda to protosulphate of iron. The *protophosphate* of iron is at first white, but soon becomes blue by exposure: it fuses and forms a crystalline bead before the blow-pipe; it is soluble in most of the acids, from which it may again be precipitated by ammonia, but it is soluble in excess of ammonia. When it has acquired a full blue tint, it is probably analogous to the *native phosphate*, and is a hydrated compound of the phosphate of the protoxide with phosphate of the peroxide. According to Kane, this *blue phosphate* is a double salt, and may be at once produced by adding phosphate of soda to the solution of the mixed sulphates of iron from which the alkalis precipitate the black (magnetic) oxide (p. 717.) The precipitate is blue and not changed by exposure to air: its formula is $\text{HO}, 2\text{FeO}, \text{PO}_5 + 2\text{Fe}_2\text{O}_3, \text{PO}_5$. The analyses of the crystallized and amorphous native phosphates agree with the formula $3\text{FeO}, c\text{PO}_5 + 8\text{HO}$. (GMELIN.)

PERPHOSPHATE OF IRON, is a white insoluble precipitate, formed by adding common phosphate of soda to persulphate or perchloride of iron.

Gmelin represents this decomposition by the following formula, $3[2\text{NaO}, \text{cPO}_5] + 2[\text{Fe}_2, \text{Cl}_3] = 6\text{NaCl} + [2\text{Fe}_2\text{O}_3, 3\text{PO}_5]$, observing, however, that it does not agree with Vogel's analysis of the salt in question. (*Ann. Phil.*, xiii. 310.) The white precipitate is rendered brown by solution of ammonia, (forming a subsalt?) but is not soluble in ammonia unless excess of the phosphate of soda be present, when it forms a brown solution which remains clear with ferrocyanide of potassium till an acid is added, when Prussian blue is thrown down. When heated it gives out water and becomes brown. Digested with potassa or soda it is converted into a brown *subperphosphate*.

Native Phosphate of Iron occurs in the form of a blue earthy powder; or if at first white, it becomes blue by exposure: it also is found in prismatic crystals. The former has sometimes improperly been termed *Native Prussian Blue*, and has been found in alluvial soil: the latter occurs with iron pyrites in Cornwall. The blue crystallized variety (Vivianite) analyzed by Stromeyer (*Untersuchungen*, i. 274), afforded 41 *per cent.* of protoxide of iron, 31 of phosphoric acid, and 28 of water. The brown radiated and nodular varieties of native phosphate of iron are hydrated phosphates of the peroxide. (GMELIN.)

IRON AND CARBON. CARBURET OF IRON. It is doubtful how far any true atomic compound of iron and carbon can be obtained. I have already adverted to the claims of *graphite* to be so considered, and in a subsequent paragraph the composition of *cast-iron*, in reference to the carbon it contains, will be noticed. It has been observed by Berzelius, that some of the combinations of oxide of iron with organic acids may possibly yield by calcination definite carburets; the residues of the calcination of Prussian blue, and of ferrocyanide of ammonium, are also combinations of iron and carbon, but how far these contain also nitrogen is a question which has not been adequately examined. By long-continued fusion of steel with charcoal, Faraday obtained a highly crystalline compound containing between 5 and 6 *per cent.* of carbon, and apparently therefore definite in its nature. All these compounds are principally interesting in reference to their influence upon the properties of cast-iron and steel. Faraday's crystalline carburet may be regarded as $\text{Fe}_4 \text{C}$.

					Faraday.
Iron	4	112	94.9
Carbon	1	6	5.1
<hr/>					
Carburet of iron	1		118		100.0

According to Berzelius (*Lehrbuch*), when the alkaline ferrocyanides are heated in close vessels the cyanide of the alkaline base is unchanged, but the cyanide of iron is decomposed, evolving nitrogen, and leaving FeC_2 . This is best obtained from ferrocyanide of ammonium. The similar ignition of pure Prussian blue leaves Fe_2C_3 .

Considerable difficulty attends the analysis of compounds of carbon and iron, in estimating the proportion of the former: this has generally been indirectly effected by ascertaining the quantity of iron, and considering the loss of weight as carbon; a method obviously objectionable. If the action of dilute sulphuric acid be resorted to, a portion of carbon is carried off by hydrogen; the same is the case with hydrochloric acid; and

if nitric acid be used, carbonic acid may be formed, and artificial tannin (humic acid) produced. Perhaps the best method is to mix 5 grains of the compound (such as cast-iron or steel) reduced to powder or fine filings, with 60 or 80 grains of chromate of lead; about a fourth part of this mixture is then put aside, and 5 grains of chlorate of potassa are added to and well mixed with the remainder; this mixture is then put into a tube similar to those used in organic analyses, and the portion of the mixture without the chlorate is afterwards put upon it; the tube is then properly adapted to Liebig's apparatus, and that portion of it is first heated which contains the mixture without the chlorate, and when this is red-hot, the heat is successively applied to the whole; in this way the whole of the carbon of the carburet is burned and converted into carbonic acid, which is absorbed by the solution of potassa in the bulb apparatus, and so weighed. (See *Organic Analysis*.) It is convenient to protect the tube by a strip of thick leaf copper folded round it in order to enable it to bear the temperature requisite for the fusion of the chromate of lead. In three experiments, 5 grains of the same cast-iron gave

0.582 carbonic acid = 3.22 of carbon per cent.

0.585 " = 3.23 "

0.588 " = 3.25 "

(REGNAULT, *Ann. Ch. et Ph.*, LXX. 107.)

PROTOCARBONATE OF IRON. FeO, CO_2 . When a solution of a pure protosalt of iron is precipitated by carbonate or bicarbonate of potassa or soda, a white *hydrated protocarbonate of iron* falls, which, if washed and dried with all the requisite precautions for excluding oxygen, forms a greenish tasteless powder, containing from 24 to 30 *per cent.* of carbonic acid: it may therefore be considered as $\text{FeO}, \text{CO}_2, \text{HO}$. When air is not excluded, the white precipitate presently passes through various shades of green, and if exposed to air becomes brown, losing carbonic acid, and passing into hydrated peroxide.

When carbonic acid in aqueous solution is digested with iron filings, a colorless solution of the protocarbonate is obtained: it is not an uncommon ingredient in mineral waters, where it is held in solution by excess of carbonic acid. The most celebrated springs of this kind in England are those of Tunbridge Wells: when boiled or when exposed to air they deposit hydrated peroxide of iron: they have an inky flavor, and are immediately blackened by vegetable astringents.

Native Protocarbonate of Iron, or Spathose Iron Ore. FeO, CO_2 , occurs in Germany, and in some parts of Cornwall, crystallized in modified rhomboids. Its primary form is a rhomboid closely resembling that of carbonate of lime. Its color is yellowish, or brownish grey. It generally contains manganese, lime, and a trace of magnesia: it slowly dissolves in hydrochloric acid, evolving carbonic acid. A specimen of this mineral from Eulenloh in Bareuth, analyzed by Bucholz (*Gehlen's Journ.*, i. 231), contained carbonic acid 36, protoxide of iron 59, lime 3, water 2. These components indicate that this mineral consists essentially of protocarbonate of iron, composed of

Protoxide of iron	1	36	62.06
Carbonic acid.....	1	22	37.94
<hr/>					
Protocarbonate of iron	1		58		100.00

The *clay iron ore* of our coal districts, from which British iron is chiefly obtained, is an impure *protocarbonate of iron*. Previous to reduction, it is reduced by heat to the state of oxide, as will appear from the account of the manufacture of iron at the end of this section. The following table shows the composition of six specimens of the clay ironstone from the coal-beds of the neighbourhood of Glasgow, analyzed by Dr. H. Colquhoun. (*Brewster's Journ.*, vii. 234.)

Carbonic acid	32·53	...	33·63	...	31·86	...	30·76	...	26·35	...	33·10
Protoxide of iron	35·22	...	45·84	...	42·15	...	38·80	...	36·47	...	47·33
Protoxide of manganese	—	...	0·20	...	—	...	0·07	...	0·17	...	0·13
Lime	8·62	...	1·90	...	4·93	...	5·30	...	1·97	...	2·00
Magnesia	5·10	...	5·90	...	4·80	...	6·70	...	2·70	...	2·20
Silica	9·56	...	7·83	...	9·73	...	10·87	...	19·20	...	6·63
Alumina	5·34	...	2·53	...	3·77	...	6·20	...	8·03	...	4·30
Peroxide of iron	1·16	...	—	...	0·80	...	0·33	...	0·40	...	0·33
Coaly matter.....	2·13	...	1·86	...	2·33	...	1·87	...	2·10	...	1·70
Sulphur	0·62	...	—	...	—	...	0·16	...	—	...	0·22
Moisture	—	...	0·99	...	—	...	—	...	—	...	—
	<hr/>			<hr/>			<hr/>			<hr/>	
	100·37		100·68		100·37		101·00		98·09		97·94

PERCARBONATE OF IRON has not been obtained in a separate state; for the protocarbonate, whilst drying, exposed to air, loses carbonic acid, and becomes peroxide. The precipitate obtained by the decomposition of protosulphate of iron by carbonate of soda, washed and dried, was formerly known in pharmacy under the name of carbonate of iron: but, as above stated, it becomes peroxide by exposure, retaining however, according to Soubeiran, a little carbonic acid: thus he found the precipitate, after exposure in thin layers to the air of a damp cellar for three months, to contain 71·4 peroxide of iron, 8·3 carbonic acid, 20· water. (*Ann. Ch. et Ph.*, xlv. 326.) When bicarbonated alkalis are digested with recently-precipitated peroxide of iron, triple salts are formed.

IRON AND CYANOGEN. These substances give rise to several important compounds, in which they exist either combined in various proportions, or as a compound radical or base, in union with other bodies.

PROTOCYANIDE OF IRON. FeCy, is obtained, according to Berzelius, in the form of a grey powder, by gently heating ammonio-cyanide of iron (Ferrocyanide of Ammonium) out of the contact of air. It is formed, according to Robiquet, by digesting recently-prepared Prussian blue in a well-stopped phial with a saturated solution of sulphuretted hydrogen; it becomes white, and the solution contains hydrocyanic acid. When solutions of cyanide of potassium and protosulphate of iron are mixed, an abundant reddish precipitate falls, which is redissolved by excess of the cyanide, and then forms ferrocyanide of potassium. Upon the whole, it is doubtful whether a pure protocyanide of iron has been isolated: its components are

Iron.....	1	...	28	...	51·9	Iron	51·9
Carbon	2	...	12	...	22·2	Cyanogen	48·1
Nitrogen	1	...	14	...	25·9		
	<hr/>			<hr/>			<hr/>
	1		54		100·0		100·0

According to Pelouze (*Ann. Ch. et Ph.*, Lxix. 40), a combination of cyanogen and iron (Fe_3Cy_4) corresponding to the black magnetic or deutoxide of iron, is obtained by passing a current of chlorine into a boiling solution of ferrocyanide of potassium; a green powder precipitates, which is to be boiled in 8 or 10 parts of concentrated hydrochloric acid, by which peroxide of iron and Prussian blue are dissolved, and a green powder remains, which, when washed and dried in vacuo, constitutes this intermediate combination, $=\text{FeCy} + \text{Fe}_2\text{Cy}_3 + 4\text{HO}$. Heated to 355° it loses water, cyanogen, and a little hydrocyanic acid, and acquires a deep purple color. In a solution of caustic potassa it is converted into peroxide of iron, and a mixture of the ferrocyanides of potassium.

PERCYANIDE OF IRON. SESQUICYANIDE OF IRON. Fe_2Cy_3 . This compound has not been isolated. It is obtained in solution when ferridcyanide of potassium is decomposed by silico-fluoride of iron, forming a brown astringent liquid; but on evaporation it deposits Prussian blue. (See *Ferridcyanides*.)

FERROCYANIDES. Two views have been taken of the constitution of these salts: upon one of these, the protocyanide of iron combines with other metallic cyanides to form double cyanides, so constituted as to contain 1 equivalent of ferrocyanide combined with 2 equivalents of the other cyanide: their elements, therefore, are in such a ratio, that if the metals were converted into *protoxides* at the expense of water, the hydrogen would just suffice to form hydrocyanic acid with the cyanogen; or, in other words, *one* equivalent of the respective ferrocyanides would decompose *three* equivalents of water.

Others apply the term *ferrocyanogen* to a hypothetical compound (salt-radical) of 3 atoms of cyanogen and 1 of iron, Fe,Cy_3 , or $\text{Fe,C}_6\text{N}_3 = \text{Cfy}$. Upon the former view the ferrocyanides would be written $2\text{MCy} + \text{FeCy}$, upon the other, $2\text{M} + \text{Cfy}$: the former appears the simpler, and therefore the preferable, view, but there are theoretical objections to its adoption.

FERROCYANOGEN, Cfy , regarded as a compound of 1 atom of iron and 3 of cyanogen, contains

Iron.....	1	...	28	...	26.41	Iron	1	...	28	...	26.41
Carbon	6	...	36	...	33.96	} = Cyanogen	3	...	78	...	73.59
Nitrogen.....	3	...	42	...	39.63						
<hr/>											
Ferrocyanogen	1		106		100.00				106		100.00

FERROCYANIDE OF HYDROGEN. FERROCYANIC ACID. HYDROFERROCYANIC ACID. FeCy_3H_2 , or Cfy,H_2 . (*Ferrochyzic acid* of Porret, by whom it was discovered. *Ann. Phil.*, Sept. 1818.) This acid may be obtained by the following processes: 1. Dissolve 58 grains of crystallized tartaric acid in alcohol, and pour the solution into a phial containing 50 grains of ferrocyanide of potassium dissolved in 3 drachms of warm water; by these means the potassa is precipitated in the state of super-tartrate, and the ferrocyanic acid remains dissolved in the alcohol, from which it may be obtained, by careful evaporation, in small cubic crystals.

(PORRETT.) 2. A solution of ferrocyanide of barium may be decomposed by sulphuric acid, so as exactly to abstract the baryta in the form of sulphate. 3. Berzelius recommends the decomposition of recently-precipitated ferrocyanide of lead or copper diffused through water, by sulphuretted hydrogen, filtering, and getting rid of the excess of sulphuretted hydrogen, which would spoil the air-pump, by a little ferrocyanide of lead: the solution should ultimately be rapidly filtered, and evaporated in vacuo over sulphuric acid: a white residue remains. 4. Mix a cold saturated solution of ferrocyanide of potassium with one-fourth its volume of strong hydrochloric acid, and agitate it with half its volume of ether: a white crystalline substance separates, which, when washed with ether and dried, or, if necessary, dissolved in alcohol, and again precipitated by ether, is ferrocyanic acid. (POSSELT.) In this decomposition, 1 atom of ferrocyanide of potassium and 2 of hydrochloric acid yield 1 of ferrocyanic acid and 2 of chloride of potassium. $K_2Cfy + 2HCl = H_2Cfy + 2KCl$. The ferrocyanic acid thus obtained is soluble in water and alcohol, and powerfully acid: it decomposes the alkaline carbonates with effervescence, forming with them ferrocyanides of their bases: though it may be atomically represented as a hydrocyanate of cyanide of iron $= FeCy, 2HCy$, it exhibits no properties in common with hydrocyanic acid or hydrocyanates; it is inodorous, and not poisonous: it is permanent in the dry state, but when moistened and long exposed to air it becomes changed into Prussian blue. It consists of

Iron.....	1	...	28	...	25.92	Iron	1	...	28	...	25.92
Carbon.....	6	...	36	...	33.33	} = Cyanogen....	3	...	78	...	72.21
Nitrogen	3	...	42	...	38.88						
Hydrogen	2	...	2	...	1.87		2	...	2	...	1.87
<hr/>						<hr/>					
Ferrocyanic acid....	1		108		100.00		1		108		100.00

Ferrocyanogen, regarded as a bibasic radical, forms two sets of salts, combining namely with 2 atoms of the same metal, as in the ferrocyanide of potassium, K_2Cfy ; or with 2 atoms of different metals, as in the ferrocyanide of potassium and calcium, K,Ca,Cfy : and when these salts are formed by the ferrocyanic acid, the 2 atoms of its constituent hydrogen are replaced by 2 atoms of the same or of different metals.

The *ferrocyanides* are decomposed by heat with various phenomena. 1. The ferrocyanogen evolves nitrogen and becomes converted into carburet of iron, which remains mixed with the basic cyanide; this is the case with *ferrocyanide of potassium*. 2. The cyanogen of both the cyanides is decomposed, nitrogen evolved, and metallic carburets of iron and of the basic metal are formed; as with *ferrocyanide of lead*. 3. The basic cyanide evolves cyanogen, and is reduced; as in the case of *ferrocyanide of silver*.

FERROCYANIDE OF POTASSIUM. PRUSSATE OF POTASSA. $K_2,FeC_6N_3 = K_2Cfy$ or $Fe,K_2,3Cy$. When iron filings are digested in a solution of cyanide of potassium, oxygen is absorbed from the air, the iron gradually dissolves, the liquor becomes alkaline from the presence of potassa, and, on evaporation, yields yellow crystals of the above compound $= K_2Cfy, 3HO$. If air be excluded, the same products are formed, but hydrogen is evolved in consequence of the decomposition of water. Under similar

circumstances, sulphuret of iron and cyanide of potassium form ferrocyanide and sulphuret of potassium.

When *Prussian blue* is boiled with potassa it is decomposed; it loses its blue color; oxide of iron is separated; and on filtering and evaporating the solution, crystals of the ferrocyanide are obtained. It is best formed by adding powdered Prussian blue (previously heated with a dilute sulphuric acid composed of 1 part of acid and 5 of water, and afterwards washed), to a hot solution of potassa, as long as its color is destroyed.

This salt is largely prepared as an article of commerce, chiefly for the use of calico-printers, by the following process: "Into an egg-shaped *iron* pot, brought to moderate ignition, project a mixture of good pearl-ash and dry animal matters, of which hoofs and horns are best, in the proportion of 2 parts of the former to 5 of the latter. Stir them well with a flat *iron* paddle. The mixture, as it calcines, will gradually assume a pasty form, during which transition it must be tossed about with much manual labor and dexterity. When the conversion into a chemical compound is seen to be completed by the cessation of the fetid animal vapors, remove the pasty mass with an iron ladle. If this be thrown, while hot, into water, some of the prussic acid will be converted into ammonia, and of course the usual product diminished. Allow it to cool, dissolve it in water, clarify the solution by filtration or subsidence, evaporate, and, on cooling, yellow crystals of the ferroprussiate of potash will form. Separate these, redissolve them in hot water, and, by allowing the solution to cool very slowly, larger and very regular crystals may be had." (URE'S *Dictionary*.)

The late Mr. Charles Macintosh, of Glasgow, one of the largest manufacturers of this salt, informed me, that the animal matters employed as the source of cyanogen are chiefly chips of horns, animal hoofs, woollen rags, and the substance called *greaves*, which is the refuse of tallow-melters, and consists chiefly of cellular membrane from which the fat has been expressed: these are burned, and, in fact, fused at a very high heat with potash, to form what is called *prussiate cake*; this, when cold, is lixiviated with water, and the evaporated solution yields a first crop of very impure salt; it is redissolved, and the second crystallization is allowed to go on very slowly, it being at least a fortnight before the contents of the coolers are disturbed. The iron requisite to the constitution of the salt is derived from the pots and stirrers used in the operation, or, if requisite, iron filings are added.

Dr. Gregory observes that the essential parts of this process are, first, the presence of as much nitrogen as possible in the animal matter; hence fresh dried uncalcined animal matter is far preferable to animal charcoal; secondly, the presence of metallic iron or sulphuret of iron; the former is either directly derived from the vessels, which are rapidly corroded, or it is added as filings; the latter is formed from the iron of the vessels by the action of bisulphuret of potassium, which arises from the decomposition by charcoal at a red-heat of the sulphate of potassa contained in the potash or pearl-ash, hence pure carbonate of potassa is not adapted to this process; thirdly, the exclusion of air, as far as possible, in order to prevent the oxidation and destruction of the cyanide of potassium formed.

The following explanation of the theory of this process is from Liebig.

When animal substances containing carbon and nitrogen are fused with potash at a red-heat, the potassium is reduced by the carbon, and forms by its reaction on the other ingredients cyanide of potassium. The fused mass at a red-heat contains no ferrocyanogen, but iron and carburet of iron in the form of a suspended powder. When it is lixiviated with cold water and immediately evaporated, it furnishes no ferrocyanide; but when the solution is gently heated for several hours in the contact of air, oxygen is absorbed, it acquires a yellow color, and now contains much ferrocyanide of potassium. This explains why a solution of cyanide of potassium in pure water, and in the presence of finely-divided metallic iron, absorbs the oxygen of the air in passing into the state of oxide of potassium and dissolving the metal; the potassium of the cyanide, in yielding to the iron the cyanogen with which it was combined, and so forming cyanide of iron, enables it to combine with the remaining undecomposed cyanide of potassium to form ferrocyanide of potassium. In close vessels the solution of iron by cyanide of potassium evolves hydrogen. The fused mass also contains free potassa, which, by being boiled with the cyanide of potassium, decomposes it into formiate of potassa and ammonia. When animal substances are fused in open vessels with potassa, cyanate of potassa is formed, which is decomposed by boiling into ammonia and bicarbonate of potassa; the quantity of ammonia formed being in proportion to the loss of cyanide of potassium. The best way of converting the whole of the cyanide into ferrocyanide of potassium, is to treat one-third of a cold solution of the raw mass with protosulphate of iron, as long as a precipitate falls, and then to add the remaining two-thirds of the solution, and heat the whole to the boiling-point; the solution may then be evaporated without decomposition, and the sulphate of potassa is easily separated by crystallization from the ferrocyanide. The original solution of the fused mass generally contains sulphuret and sulphocyanide of potassium, and formiate and carbonate of potassa, which remain in the mother-liquor.

Mr. L. Thompson has observed that cyanide of potassium is abundantly formed when an ignited mixture of coke or charcoal, carbonate of potassa, and iron filings, is exposed to the action of the air. In that process he says the potassa is decomposed by the iron, and that the evolved potassium combines with carbon and with the nitrogen of the atmosphere; and that the cyanide of potassium results from this action. He proposes to apply this process to the manufacture of Prussian blue. (*Trans. Soc. Arts.*, Lii. 24.)

Ferrocyanide of potassium forms permanent lemon-yellow crystals, of the specific gravity of 1.83: they are insoluble in alcohol, which throws down the salt in yellow flakes from its aqueous solution. Water at 60° takes up about one-third, and at 212°, its own weight of this salt. (URE.) According to others it is soluble in 4 of cold and 2 of boiling water. It has a bitter, saline, and sweetish taste, and is not poisonous. The large crystals are tough, and the thin ones somewhat elastic: their forms have been described by Levy and by Brooke. (*Quart. Journ.*, xv. 288; *Ann. of Phil.*, N. S., vi. 41.) They are four-sided tables, derived from a primary octohedron. When moderately heated they lose color, and crumble into powder, parting with about 13 *per cent.* of water, but they retain their figure till upon the verge of ignition. By a red-heat this salt is converted,

with the escape of nitrogen, into carburet of iron and cyanide of potassium: and in the presence of air the latter salt becomes cyanate of potassa, and the iron is oxidized. Boiled with dilute sulphuric or hydrochloric acid, hydrocyanic acid is given out, and a white precipitate formed similar to that which the salt produces in a solution of protosulphate of iron. By nitric acid and by chlorine it is converted into ferridecyanide of potassium. The action of concentrated sulphuric acid upon this salt is attended by the evolution of pure carbonic oxide, and the production of an anhydrous salt (an iron alum,) containing 2 atoms of peroxide of iron, 1 of potassa, 1 of oxide of ammonium, and 5 of sulphuric acid, represented by the formula $2\text{Fe}_2\text{O}_3, 3\text{SO}_3 + \text{KO}, \text{SO}_3; \text{NH}_4\text{O}, \text{SO}_3$. (FOWNES, *Chem. Gaz.*, June, 1843.)

Neither sulphuretted hydrogen, the hydrosulphurets, the alkalis, nor tincture of galls, produce any precipitate in solutions of this salt. Red oxide of mercury decomposes it at a moderate heat, peroxide of iron and metallic mercury are precipitated, and *cyanide of mercury* formed; so that the iron is peroxidized at the expense of the oxide of mercury.

When a solution of this salt forms insoluble precipitates in metallic solutions, the nature of the metal present may often be judged of by the character and color of the precipitate, as indicated by the following table:

MANGANESE	Neutral protochloride	White
IRON	Neutral protosulphate	White or pale blue
Ditto	Perchloride	Prussian blue
ZINC	Chloride	Yellowish white
TIN	Acid protochloride	White, then yellow and bluish
Ditto	Acid perchloride	Pale yellow
CADMIUM	Chloride	White
COPPER	Protochloride	Lilac
Ditto	Pernitrate	Deep brown
LEAD	Nitrate	White
ANTIMONY....	Tartrate of antimony and potassa	0
BISMUTH	Tartrate of bismuth and potassa	0
COBALT	Chloride	Pale green
URANIUM	Sulphate	Deep brown
TITANIUM	Acid chloride	Deep blue (from acid)
Ditto	Neutral sulphate	Sap green
ARSENIC.....	White oxide	0
Ditto	Arsenic acid	0
NICKEL	Sulphate	Grey
MERCURY	Acid nitrate	Greenish white
Ditto	Acid pernitrate	Ditto
Ditto	Corrosive sublimate	White
PALLADIUM	Chloride	Olive
SILVER	Nitrate	Cream-colour
GOLD	Chloride	0
PLATINUM....	Chloride	Yellow

It is obvious that various views may be entertained in respect to the proximate constitution of this salt: its ultimate elements, in its anhydrous state, are

Potassium	2	...	80	...	43·01
Iron	1	...	28	...	15·05
Carbon	6	...	36	...	19·35
Nitrogen	3	...	42	...	22·59
<hr/>					
Anhydrous ferrocyanide of potassium.....	1		186		100·00

These may be arranged as follows:

Potassium.....	2	...	80	...	43.01	Cyanide of potassium	2	...	132	...	70.9
Ferrocyanogen....	1	...	106	...	56.99	Cyanide of iron	1	...	54	...	29.1
	1		186		100.00		1		186		100.0
Potassium	2	...	80	...	43.01						
Iron	1	...	28	...	15.05						
Cyanogen	3	...	78	...	41.94						
	1		186		100.00						

And the *hydrated* or *crystallized ferrocyanide* will consist of

						Ure.	Döbereiner.		
Anhydrous ferrocyanide of potassium	1	...	186	...	87.3	...	87.12	...	88
Water	3	...	27	...	12.7	...	12.88	...	12
Crystallized ferrocyanide of potassium	1		213		100.0		100.00		100

So that, in the crystallized salt, the oxygen and the hydrogen of the water are exactly in such proportions as are required to convert the metals into protoxides, and the cyanogen into hydrocyanic acid.

BIFERROCYANIDE OF POTASSIUM. When a mixture of the preceding ferrocyanide of potassium with dilute sulphuric acid is subjected to distillation, hydrocyanic acid is evolved, and a ferrocyanide, represented by the formula, $2\text{FeCy}, \text{Kcy}$, is among the products. Everitt termed this ferrocyanide "yellow salt," in the following diagram, showing the changes which ensue when 6 atoms of concentrated sulphuric acid are heated with 2 atoms of crystallized ferrocyanide of potassium. (PHILLIPS, *Translation of London Pharmacopœia*.)

Before Distillation.				After Distillation.				
	Atoms.	Equivalents.			Atoms.	Equivalents.		
Sulphuric acid.....	6	...	240	} = {	Bisulphate of potassa....	3 384	
Cyanide of potassium....	4	...	264		Hydrocyanic acid	3 81	
Cyanide of iron	2	...	108		Cyanide of potassium....	1	} Yellow Salt { 66	
Water { 6 in the acid }	12	...	108		Cyanide of iron	2		} 108
					Water.....	9		
<hr/> 720					<hr/> 720			

According to Gay Lussac, the result of the action of sulphuric acid upon ferrocyanide of potassium is a *white* powder, which, after having been well washed with boiling water, and exposed to air, acquires a dingy blue tint, but becomes deep blue when moistened by dilute sulphuric acid, and yields sulphate of potassa: this *white ferrocyanide* consists, he says, of 7 atoms of iron, 2 of potassium, and 9 of cyanogen: by the dilute acid, the 2 atoms of potassium are abstracted, and the remaining 7 of iron and 9 of cyanogen form Prussian blue. (*Ann. de Ch. et Ph.*, XLvi. 78.) The components of the ferrocyanide appear from Everitt's statement to be 3 atoms of cyanogen, 2 of iron, and 1 of potassium, so that its formula would be KFeCy_3 , if considered as containing ferrocyanogen; an atom of potassium being replaced by one of iron.

FERROCYANIDE OF AMMONIUM. FERROCYANATE OF AMMONIA. When ferrocyanide of lead is diffused through water holding carbonate of ammonia in solution, or when Prussian blue is digested in solution of ammonia, the filtered liquors yield small yellow octohedral crystals, which

are transparent, permanent in the air, very soluble in water, and insoluble in alcohol. By boiling in water this salt is converted into cyanide of ammonium and cyanide of iron. When equal parts of ferrocyanide of potassium and sal-ammoniac are boiled together in 6 parts of water, large brittle crystals of a lemon-yellow color are deposited on cooling, composed, according to Bunsen, of 1 equivalent of ferrocyanide of ammonium, 1 of sal-ammoniac, and 3 of water.

The constituents of the crystals of ferrocyanide of ammonium appear to be

Iron.....	1	28	16·8
Ammonium.....	2	36	20·4
Cyanogen	3	78	46·6
Water	3	27	16·2
<hr/>					
Crystals of ferrocyanide of ammonium.....	1		167		100·0

FERROCYANIDE OF SODIUM. $2\text{Na},\text{Cfy}$: or $2\text{NaCy},\text{FeCy}$. This salt is obtained by boiling Prussian blue with caustic or carbonate of soda. Its solution yields hydrated yellow quadrangular prismatic crystals, soluble in 4·5 of water at 55° , and insoluble in alcohol. They effloresce, and lose by drying 40 *per cent.* of water. Their components are

Iron	1	28	10·7
Sodium.....	2	48	18·3
Cyanogen	3	78	29·8
Water	12	108	41·2
<hr/>					
Crystals of ferrocyanide of sodium....	1		262		100·0

FERROCYANIDE OF BARIUM, $2\text{Ba},\text{Cfy}$: or $2\text{BaCy},\text{FeCy}$, is obtained by digesting Prussian blue in hot baryta water: as it cools, yellow rhomboidal prisms are deposited. This salt requires 100 parts of boiling water and 1920 of cold water for its solution: its crystals contain 18 *per cent.* or 6 equivalents of water, of which the greater part may be expelled at 212° .

FERROCYANIDE OF STRONTIUM, $2\text{Sr},\text{Cfy}$: or $2\text{SrCy},\text{FeCy}$, is formed by boiling a mixture of Prussian blue and hydrate of strontia in water: it forms yellow crystals soluble in 4 parts of cold water.

FERROCYANIDE OF CALCIUM. $2\text{Ca},\text{Cfy}$: or $2\text{CaCy},\text{FeCy}$. When hydrate of lime and Prussian blue are boiled in water, and the resulting solution filtered and evaporated to the consistence of syrup, it yields large lemon-yellow four-sided prisms, which effloresce in a warm atmosphere, and at 212° lose nearly 40 *per cent.* of water, retaining about 2 *per cent.* which cannot be separated except at a higher temperature.

FERROCYANIDE OF MAGNESIUM, $2\text{Mg},\text{Cfy}$: or $2\text{MgCy},\text{FeCy}$, crystallizes in small deliquescent tables.

FERROCYANIDE OF MANGANESE. $2\text{Mn},\text{Cfy}$, or $2\text{MnCy},\text{FeCy}$. A white precipitate formed by adding ferrocyanide of potassium to a soluble protosalt of manganese: it acquires a red tint by exposure: it is never quite free from potassium: it is soluble in acids.

FERROCYANIDE OF IRON. When ferrocyanide of potassium is added to a pure protosalt of iron a white precipitate falls, which, if the potassium of the precipitant were entirely replaced by iron, would be a proto-cyanide of iron, or, at least, isomeric with it, for $K_2Cfy + 2FeO = Fe_2Cfy + 2KO$; and $Fe_2Cfy = Fe_3Cy_3$; but Proust has shown that the precipitate (which at first is white, but soon becomes blue by exposure) contains potassium, and Berzelius considers it as identical with the white salt above adverted to (p. 740), as formed in the process for obtaining hydrocyanic acid by the distillation of ferrocyanide of potassium with sulphuric acid, and which we have before termed a biferrocyanide of potassium. The same salt is thrown down on adding hydrochloric acid to a solution of ferrocyanide of potassium. (See Gay Lussac's remarks, cited at p. 740). Representing this salt by the formula $KFeCfy$, it comes under the class of *ferrocyanides with two basic metals*, noticed further on.

SESQUIFERROCYANIDE OF IRON. PRUSSIAN BLUE. This celebrated pigment was accidentally discovered by Diesbach, a color-maker at Berlin, in the year 1710: the first description of the mode of preparing it is given by Woodward, in the *Philosophical Transactions* for 1724. It is largely consumed in the decorative arts; it is extensively employed as a dye-stuff, and in calico-printing; it is used in making some of the varieties of what is called *stone-blue*, and is sometimes added to starch, though for this purpose, as well as for covering the yellow tint of paper, smalt or cobalt blue is preferable. Prussian blue was formerly made as follows: Equal parts of carbonate of potassa and some animal substance, such as dried blood, or horn-shavings, were heated red hot, in a crucible, for half an hour, and 6 or 8 parts of water poured upon the mixture when it had quite cooled. This solution, formerly called *lixivium sanguinis*, was filtered and mixed with a solution containing 2 parts of alum and 1 of protosulphate of iron; a precipitate fell, at first of a dingy-green hue, but which, by copious washings with very dilute hydrochloric acid, acquired a fine blue tint.

At present, Prussian blue is prepared of different degrees of purity, by precipitating solutions of peroxide of iron by ferrocyanide of potassium, various additions being made to it according to the purposes for which it is required. *Pure Prussian blue* is obtained by adding a solution of ferrocyanide of potassium to persulphate of iron, thoroughly washing the precipitate, first with water slightly acidulated by sulphuric acid, and then with pure water, and ultimately drying it in a warm place. Liebig recommends the following process on the authority of Hochstätter: Dissolve 6 parts of protosulphate of iron and 6 parts of ferrocyanide of potassium, each separately, in 15 parts of water; mix the two solutions, and add to them 1 part of concentrated sulphuric, and 24 of hydrochloric acid, under constant stirring. After some hours, add a clear solution of 1 part of chloride of lime in 80 of water, in successive portions, taking care to stop as soon as any chlorine escapes by effervescence. After some hours, the precipitate should be thoroughly washed, and dried either at common or higher temperatures. The finest product is obtained by washing the precipitate with dilute nitric acid.

Prussian blue is of a peculiarly rich and intense blue, with a copper tint upon its surface: it is insipid, inodorous, insoluble in water, in

alcohol, and in dilute acids, and is not poisonous. Concentrated sulphuric acid forms with it a white pasty mass, from which water again separates it unaltered; nitric acid decomposes it; concentrated hydrochloric acid ultimately abstracts part of its iron. Sulphuretted hydrogen, and iron and zinc filings render it white, in consequence of the abstraction of part of its cyanogen. The alkalis decompose it into soluble ferrocyanides and oxide of iron, hence, as a dyeing material, it does not resist the action of soap. Boiled in water with peroxide of mercury, it forms cyanide of mercury, and an insoluble compound of cyanide and oxide of iron. According to Chevreul, Prussian blue becomes white in the direct rays of the sun, but regains its blue color in the dark. It is occasionally used in the composition of writing fluids, and forms the basis of Stephens' blue ink, in which it is said to be held in solution by oxalic acid. It is extremely hygrometric, and after having been well dried, speedily attracts moisture. When subjected to destructive distillation, it yields a little water and hydrocyanate of ammonia, and then carbonate of ammonia, and a black carburet of iron remains in the retort.

Prussian blue is regarded as a compound of cyanogen and iron, but various views have been taken of its atomic constitution, according as it has been considered, as containing or not containing the elements of water. From the researches of Berzelius, it appears, if considered as anhydrous, or merely retaining adventitious water, to be constituted of

Iron	7	...	196	...	45·6
Cyanogen	9	...	234	...	54·4
	<hr/>		<hr/>		<hr/>
	1		430		100·0

The *ultimate elements*, therefore, of anhydrous Prussian blue, are

Iron	7	...	196	...	45·6
Carbon	18	...	108	...	25·1
Nitrogen	9	...	126	...	29·3
	<hr/>		<hr/>		<hr/>
	1		430		100·0

If, therefore, it be considered as resulting from the mutual reaction of 3 atoms of ferrocyanide of potassium and 2 of peroxide of iron, it will contain 3 atoms of ferrocyanogen and 4 of iron, that is, $3 [K_2, Cfy] + 2 [Fe_2, O_3] = 6 [KO] + Fe_4, Cfy_3$. In reference to this view of the constitution of Prussian blue, it may be observed, that ferrocyanogen being bibasic, is equivalent to O_2 , and consequently Fe_4, Cfy_3 is equivalent to $2 [Fe_2O_3]$ or to Fe_4O_6 . Prussian blue therefore corresponds under this aspect with the sesquioxide and sesquichloride of iron, Fe_2O_3 , or Fe_2Cl_3 , the O_3 or Cl_3 being replaced by $Cfy_1 \frac{1}{2}$; for $Fe_2Cfy_1 \frac{1}{2} = Fe_4Cfy_3$. "It must be admitted," says Dr. Gregory, "to be a very strong argument in favour of the existence of ferrocyanogen as a bibasic radical, according to the theory of Liebig, that Prussian blue, on all other theories, the most complex and anomalous compound in the whole range of chemistry, becomes quite normal, and one of a series." The following diagram represents this view of the formation of Prussian blue, with the atomic weights of the respective bodies.

PRUSSIAN BLUE.

6 atoms of Potassa $48 \times 6 = 288$			
3 atoms of Ferrocyanide of Potassium $186 \times 3 = 558$.	6 atoms of Potassium $40 \times 6 = 240$	6 atoms of Oxygen $8 \times 6 = 48$	2 atoms of Sesquioxide of Iron $80 \times 2 = 160$
	3 atoms of Ferrocyanogen $106 \times 3 = 318$	4 atoms of Iron $28 \times 4 = 112$	
	1 atom of Prussian blue = 430		

Iron	4	112	26·05
Ferrocyanogen	3	318	73·95
<hr/>					
Prussian blue	1		430		100·00

The above statement, therefore, represents Prussian blue as an anhydrous compound of ferrocyanogen and iron; but it is generally admitted that it cannot practically be obtained in this state, and that it always contains water, or the elements of water, which cannot be expelled without the decomposition of the compound; if so, it must probably be a hydroferrocyanate of sesquioxide of iron $= 2[\text{Fe}_2\text{O}_3] + 3[\text{CfyH}_2] = 1$ atom of anhydrous Prussian blue + 6 atoms of water: or as follows:

Sesquioxide of iron....	2....	160....	33·06	}	= {	Anhydrous Prussian blue	1....	430....	88·9
Hydroferrocyanic acid	3....	324....	66·94			Water	6....	54....	11·1
<hr/>									
Hydrated Prussian	}	1	484	100·00			1	484	100·0
blue									

FERROCYANIDES WITH TWO BASIC METALS. Ferrocyanide of potassium combines with other ferrocyanides to form a peculiar class of double salts, or salts in which 1 atom of its constituent potassium is replaced by 1 atom of another metal. There are compounds of this kind with calcium, barium, strontium, magnesium, manganese, and iron; also with zinc, copper, and silver.

FERROCYANIDE OF POTASSIUM AND CALCIUM. K_2Cfy , or $[\text{K}_2\text{Cfy} + \text{Ca}_2\text{Cfy}]$ falls gradually in the form of a white crystalline powder, on mixing concentrated solutions of ferrocyanide of potassium and chloride of calcium. $\text{K}_2\text{Cfy} + \text{CaCl} = \text{KCl} + \text{KCaCfy}$. This salt is soluble in 795 parts of water at 60° , and in 145 parts at 212° . When dried at a high temperature, it burns like tinder into a mixture of oxide of iron with the cyanates of potassa and of lime. (CAMPBELL.) The solution of this salt in boiling water is yellow; by exposure to air it gradually becomes green and red from the deposition of oxide of iron, and cyanides are formed. (BERZELIUS.)

FERROCYANIDE OF POTASSIUM AND BARIUM. KBaCfy , crystallizes out of the mixed hot solution of the two ferrocyanides; the crystals are

small, and require 36 of cold and 12 of boiling water for solution. They contain 11.19 *per cent.* of water. (MOSANDER. DUFLOS.)

FERROCYANIDE OF POTASSIUM AND MAGNESIUM. KMgCfy , falls on mixing concentrated solutions of ferrocyanide of potassium and a magnesian salt: it dries into a white powder soluble in 1575 of cold and 238 of boiling water. The latter solution is yellow, forms no deposit, becomes greenish by exposure to air, and then red from deposition of oxide of iron, a cyanide being at the same time formed. (BERZELIUS.)

FERROCYANIDE OF POTASSIUM AND MANGANESE. KMnCy . When a solution of a protosalt of manganese is dropped into a solution of ferrocyanide of potassium, a grey precipitate falls, which becomes blue by exposure. If the solution of ferrocyanide of potassium be dropped into that of the salt of manganese, the white or pinkish precipitate is always slightly contaminated by the double salt: it contains about 3 *per cent.* of potassium. (MOSANDER.)

FERROCYANIDE OF POTASSIUM AND IRON. It has already been observed that the white precipitate resulting from the action of ferrocyanide of potassium upon a protosalt of iron contains potassium, and that its constitution has been variously represented. Liebig, upon the authority of Berzelius's analysis, considers it as a compound of 3 atoms of iron and 1 of potassium, with 2 of ferrocyanogen. (Fe_3KCy_2 .) Of the 4 atoms of potassium contained in 2 of ferrocyanide of potassium, 3 are replaced by 3 of iron to form the white precipitate, while the 3 of potassium unite with the former radical of the salt of iron. Thus (in the decomposition of 3 atoms of protochloride of iron by 2 of ferrocyanide of potassium) $3[\text{FeCl}] + 2[\text{K}_2\text{Cy}] = [\text{Fe}_3\text{KCy}_2] + 3[\text{KCl}]$. The white precipitate blues by exposure, and absorbing oxygen yields ferrocyanide of potassium when washed, and after the soluble matters are thus dissolved out of it, a blue *basic sesquiferrocyanide of iron* (basic Prussian blue) remains. If the washing, however, be continued, the whole of the precipitate may be gradually dissolved, furnishing a dark blue liquor, which may be evaporated to dryness without decomposition. The blue liquor is not precipitated by alcohol, but when solution of sulphate of potassa (and certain other salts) is added, it deposits a blue flocculent precipitate, again perfectly soluble in pure water. Liebig represents the soluble blue compound by the formula $\text{Fe}_4\text{3Cy} + \text{Fe}_2\text{O}_3$, which corresponds to a compound of 1 atom of Prussian blue and 1 of sesquioxide of iron. The presence of a strong acid prevents the formation of this soluble blue compound by abstracting the peroxide of iron, and leaving Prussian blue.

Compound of ferrocyanide of potassium with Prussian blue. The blue precipitate which falls on adding a persalt of iron to solution of ferrocyanide of potassium always contains a variable quantity of ferrocyanide of potassium when the salt of iron is in excess. By repeated washing the precipitate may be deprived entirely of ferrocyanide of potassium, but it is a troublesome process, and hence it is that the Prussian blue of commerce is never free from potassium, containing from 2 to 9 *per cent.* If, in preparing Prussian blue, the ferrocyanide of potassium be in

excess, the precipitate consists of a mixture of Prussian blue with an atomic combination of Prussian blue and ferrocyanide of potassium = $\text{Fe}_2, \text{K}, 2\text{Cfy}$, or rather $\text{Fe}_4, \text{Cfy}_3 + \text{K}_2, \text{Cfy}$. This compound dissolves when the precipitate is washed, forming a deep blue liquor, which may be evaporated to dryness without decomposition: on adding foreign salts to it, it is precipitated, but it always remains soluble in pure water; it is distinguished from the preceding *basic Prussian blue* by being precipitated from its solutions by alcohol, which that compound is not. (LIEBIG.)

FERRIDCYANOGEN. $\text{Fe}_2, \text{Cy}_6 = \text{Cfdy}$. This assumed tribasic salt radical has not been isolated: it is isomeric with ferrocyanogen, being formed by the coalescence of 2 atoms of that compound: its elements are

Iron.....	2	...	56	...	26.41	Iron.....	2	...	56	...	26.41	
Carbon	12	...	72	...	33.96	} = Cyanogen	...	6	...	156	...	73.59
Nitrogen.....	6	...	84	...	39.63							
<hr/>												
Ferridcyanogen	1		212		100.00			1		212		100.00

FERRIDCYANIDE OF HYDROGEN. FERRIDCYANIC ACID. HYDROFERRIDCYANIC ACID. $\text{Fe}_2, \text{Cy}_6, \text{H}_3$; or Cfy_2, H_3 ; $= \text{Cfdy}, \text{H}_3$. This acid is prepared by decomposing recently precipitated ferridcyanide of lead by dilute sulphuric acid or by sulphuretted hydrogen: by filtration, a yellow liquor is obtained, which by very slow spontaneous evaporation deposits crystals; if heat be used, a brown powder remains: its aqueous solution gradually decomposes, especially if heated, and deposits a blue crystalline powder. Its elements are

Iron	2	...	56	...	26·05	Iron	2	...	56	...	26·05
Carbon	12	...	72	...	33·49	} Cyanogen ...	6	...	156	...	72·56
Nitrogen	6	...	84	...	39·07						
Hydrogen.....	3	...	3	...	1·39	Hydrogen ...	3	...	3	...	1·39
<hr/>											
Ferridcyanic acid	1		215		100·00		1		215		100·00

This acid, in combining with metallic oxides, produces water and a metallic ferridcyanide, its hydrogen being replaced by the metal: its compounds with the metals of the alkalis and alkaline earths are soluble in water: the others are insoluble, and are formed by the reaction of a soluble ferridcyanide upon solutions of the metallic salts.

FERRIDCYANIDE OF POTASSIUM. When chlorine is passed through a solution of ferrocyanide of potassium till the liquor ceases to precipitate Prussian blue from the *persalts* of iron, and if it be then filtered and slowly evaporated, it furnishes right rhombic prismatic crystals, which, purified by a second solution, assume a ruby-red color; they are anhydrous, and require 3.8 parts of cold water for solution, and are nearly insoluble in alcohol. They burn with brilliant scintillations, and when heated in close vessels, give off cyanogen and nitrogen, and leave ferrocyanide of potassium and carburet of iron. When dissolved in water, this salt is decomposed by sulphuretted hydrogen, sulphur and cyanide of iron are precipitated, and hydrocyanic acid and ferrocyanide of potassium formed. This salt occasions no precipitate in solutions of iron containing the peroxide only, but it is a most delicate test of the *protoxide*, with which it forms a blue precipitate. It is constituted of

Potassium	3	120	36·14
Ferridcyanogen	1	212	63·86
<hr/>					
Ferridcyanide of potassium.....	1		332		100·00

The ultimate elements of the salt are

Potassium	3	20	36·14
Iron	2	56	16·87
Carbon	12	72	21·68
Nitrogen	6	84	25·31
<hr/>					
Ferridcyanide of potassium	1		332		100·00

Although the action of chlorine furnishes the readiest mode of converting ferrocyanide into ferridcyanide of potassium, there are other agents by which the same change may be effected. (SMEE, *Phil. Mag. and Ann.*, Sept. 1840.)

The *ferridcyanides of sodium, barium and calcium*, may be obtained by the same process, care being taken to avoid excess of chlorine, which is apt to react upon the salt.

Ferridcyanide of potassium throws down the following metals, of the annexed colors.

Titanium.....	Brownish yellow	Silver	Orange-yellow
Uranium	Reddish brown	Mercury	Yellow (both oxides)
Manganese	Brownish grey	Tin	White
Cobalt	Dark red-brown	Zinc	Orange
Nickel.....	Yellowish brown	Bismuth	Yellow-brown
Copper.....	Dirty yellow-brown		

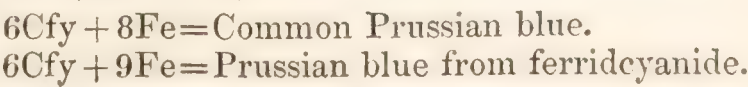
FERRIDCYANIDE OF IRON. Fe_3Cfdy ; or $\text{Fe}_3[\text{Cy}_6\text{Fe}_2]$ This is the precipitate formed by adding solution of ferridcyanide of potassium to a protosalt of iron; it is produced by the substitution of 3 atoms of iron for the 3 of potassium: it is known in commerce as *Turnbull's blue*. It may also be prepared by adding to a protosalt of iron a mixture of ferrocyanide of potassium and chloride of soda, to which hydrochloric acid has been previously added. It is distinguished from common Prussian blue by its action on ferrocyanide of potassium, for when boiled in a solution of the latter salt, it decomposes it into ferridcyanide, which is dissolved, and into an insoluble grey residue of ferrocyanide of iron and ferrocyanide of potassium. (CAMPBELL.) It consists of

Iron	3	84	28·37
Ferridcyanogen	1	212	71·63
<hr/>					
Ferridcyanide of iron	1		296		100·00

Its ultimate elements are

Iron	5	140	47·29
Carbon	12	72	24·34
Nitrogen	6	84	28·37
<hr/>					
Ferridcyanide of iron	1		296		100·00

The weight of iron in the common Prussian blue is to that in the ferridcyanide (*Turnbull's blue*) as 14 to 15, as is evident from the following formulæ. (TURNER.)



MELLONIDES OF IRON. The protomellonide is thrown down as a pale grey, and the permellonide as a dark yellow precipitate. (LIEBIG.)

SULPHOCYANIDES OF IRON. A *protosulphocyanide* $= \text{Fe}, \text{Cy}, \text{S}_2$ is formed by digesting iron in hydrosulphocyanic acid: the solution is pale bluish-green, but becomes blood-red, and deposits oxide when exposed to air. It has not been obtained in a solid form. (BERZELIUS.)

Persulphocyanide of Iron $= 2\text{Fe}, 3[\text{CyS}_2]$ Hydrosulphocyanic acid is so easily decomposed by peroxide of iron, that when filtered, it often acquires a red tint from traces of iron in the filtering paper. The red color of this compound is so intense, as to render it a most delicate test of the presence of iron in the state of peroxide; and it may be used to indicate the slightest traces of that oxide in solutions of the protosalts, taking care that air be excluded. This sulphocyanide is best obtained by digesting hydrated peroxide of iron in aqueous hydrosulphocyanic acid, and evaporating in vacuo. It forms a red deliquescent mass soluble in alcohol: both its aqueous and alcoholic solution, when evaporated in the air, absorb oxygen, depositing a basic persalt, whilst a protosulphocyanide and protosulphate of iron remain in solution. (BERZELIUS.) When the red solution of this salt is so exposed to the sun, that the rays pass through the glass jar containing it, it is rendered colorless, but the color is retained or restored when the rays pass directly from the air into the fluid: so that when a properly diluted solution is placed in a cylindrical glass vessel in direct sunshine, it loses color in the morning till about eleven in the forenoon, when the rays beginning to fall upon the surface exposed to the air, gradually restore the color, which attains its maximum about two o'clock. The salt is most readily bleached by the green rays, and it appears generally as if the colored rays were most effective in destroying their complementary tints. (GROTHUS.) In these cases the sulphocyanogen appears to be partially decomposed, and a protosulphocyanide formed in the solution, which the air again partly restores to the state of persalt, the continuance of these changes of color terminating in the decomposition of the sulphocyanide. (MEITZENDORFF. *Berzelius' Lehrbuch.*)

BORURET OF IRON. A compound of boron and iron results from the action of hydrogen at a red heat upon borate of iron. (LASSAIGNE.) According to Arfwedson, the boracic acid is not susceptible of such decomposition.

PROTOBORATE OF IRON is an insoluble yellowish powder, obtained by adding a solution of borate of soda to protosulphate of iron. (SCHEELÉ.) According to Tünnermann the precipitate is greenish, and the whole of the acid may be washed out of it.

PERBORATE OF IRON is yellow and insoluble. It is formed by adding borate of soda to persulphate of iron: it is vitrifiable at a high heat. (BERZELIUS.)

ALLOYS OF IRON. *Iron and Potassium* form a white soft alloy which effervesces in water. When a mixture of charcoal, iron-filings, and magnesia is exposed to its fusing heat, the resulting globule contains

traces of *magnesium*. With lime no analogous effect ensues. The alloy of *iron and manganese* is white, hard, and brittle, and sometimes by its presence confers peculiar characters and a damasked appearance on steel. A little iron in manganese diminishes its tendency to oxidizement. Iron containing 22 *per cent.* of manganese is no longer magnetic. (MUSSET.)

The general characters of the ferrous and ferric salts have already been enumerated at pages 714 and 716.

None of the metals precipitate iron in a metallic state, if we except zinc and cadmium, which effect an imperfect precipitation, especially from some of its protosalts, in vessels excluded from the access of air. Before the blow-pipe, peroxide of iron produces with microcosmic salt, or borax, in the exterior flame, a glass, which is blood-red while hot, but yellow when cold. The protoxide forms with these fluxes a green glass, which, by increasing the proportion of the oxide, passes through bottle-green to black, and is opaque. The glass from the peroxide becomes green in the interior flame, and is reduced to protoxide, and becomes attractable by the magnet. When placed on the wick of a candle, it burns with the crackling noise peculiar to iron.

The separation of iron from other metals may in many cases be effectually attained by the following process, first suggested by Herschel (*Phil. Trans.*, 1821, p. 293): "The solution containing iron is to be brought to the maximum of oxidation by boiling with nitric acid, it is then to be just neutralized, *while in a state of ebullition*, by carbonate of ammonia. The whole of the iron, to the last atom, is precipitated, and the whole of the other metals present (which I suppose to be manganese, cerium, nickel, and cobalt) remains in solution." (See also paper on this subject by Liebig, *Ann. Ch. et Ph.*, Nov. 1831.) In analytical operations iron is almost always weighed as peroxide.

The separation of protoxide from peroxide of iron, when existing together in solution, may be effected by boiling with carbonate of baryta; the persalt only is decomposed, and the filtered solution contains the protosalt.

MANUFACTURE OF IRON AND STEEL. It has already been stated that the nodular argillaceous carbonated iron-ore of the coal formation, is chiefly resorted to in this country as the source of the metal; the following is an outline of the process of reduction. (AIKIN'S *Dictionary; Supplement to the Encyclopædia Britannica*; LARDNER'S *Cyclopædia*; DUMAS, *Chimie app. aux Arts*.)

The first process that the ore undergoes after it has been broken into small pieces, is *roasting*. This is performed as follows: Upon an oblong piece of firm and level ground is laid a bed of small coal, from four to eighteen inches thick; upon this is placed a stratum of ironstone, from eighteen inches to two feet thick, the upper surface of which is rendered more compact by filling up the interstices with smaller pieces. Upon this rests a layer of small coal not more than two inches thick, and on this, as a base, is reared a gradually-diminishing pile of ore; finally, the whole external surface receives a complete covering of small coal and coal dust. The pile is kindled by applying burning coals to the lower stratum. The breadth of the pile at the bottom varies from ten to sixteen feet, the usual height is about five feet, and the length varies from thirty

feet to sixty yards. When the coals are consumed, the pile gradually cools, and in eight or ten days may be wheeled away to the furnace. The ore, if well roasted, will now be of a reddish-brown color, of diminished specific gravity, and will have become magnetical; the sulphur, water, inflammable matter, and carbonic acid, that it originally contained, will have been dissipated, and it is now ready to be *smelted*. The *smelling-furnace* resembles externally a truncated quadrilateral pyramid of considerable height in proportion to its thickness; it is built of strong masonry, with contrivances to obviate the danger of its cracking by the expansion that takes place when it is heated. The interior of the furnace consists of the five following parts, reckoning from the bottom upwards. The *hearth*, composed of a single block of quartz-grit about two feet square: upon this is erected what in France and Germany is called the *crucible*, which is a four-sided cavity six feet six inches high, slightly enlarging upwards so as to be two feet six inches square at the top: the part above, called the *boshes*, is in the shape of a funnel or inverted cone, eight feet in perpendicular height, and twelve feet in diameter at the top; this terminates in the *cavity* of the furnace, which is of a conical figure, thirty feet high, and three feet diameter at the top; from this part it enlarges into a funnel-shaped *chimney*, about eight feet high, and sixteen in diameter at its mouth. About two feet above the hearth is a round aperture, called the *Tuyere* or *Tweer*, made in one of the sides of the crucible to admit the extremity of the blast-pipe, through which the air in a high state of compression is forced into the furnace; and at the bottom of the crucible is an aperture, through which the scoriæ and melted metal are from time to time discharged. A furnace of this construction, if it meets with no accident, may be kept in constant work for three years or more without requiring any repairs. The furnace is charged at the chimney, by regular intervals, with coke, iron-ore, and limestone, in the proportion of about four of the first, three and one-third of the second, and one of the third, by weight, care being taken so to regulate the frequency of the charges, as that the furnace shall be always full nearly to the top of the great cavity. The density of the blast and the form of the discharging-pipe are ordered so that the chief focus of heat is about the bottom of the boshes; hence the ore has to descend about thirty-eight feet perpendicular, before it arrives at the place where the fusion is effected. This does not happen in less than forty-eight hours; so that the ore is all this time in a state of cementation at a high temperature, in contact with the burning fuel, and, in consequence, is almost saturated with carbon when it reaches the hottest part of the furnace. Being arrived at this place, the limestone flux, and the earthy particles of the coke and ore, run down into a slag*; the iron is also melted, and more or less decarbonized, and in part oxidated by the blast, inversely according to the proportion of fuel with which it is mixed. The fluid mass soon sinks down below the influence

* The *slag* chiefly consists of silica in combination with lime, alumina, magnesia and the protoxides of manganese and iron. According to Mitscherlich (*Ann. Ch. et Ph.*, xxiv.), it frequently consists of a bisilicate of lime and magnesia with more or less protoxide of iron; and this compound even

forms crystals resembling *pyroxene*. The production of *artificial minerals* by these processes, is a subject of extreme interest and importance, both in a geological and chemical view, and an excellent field for experimental inquiry.

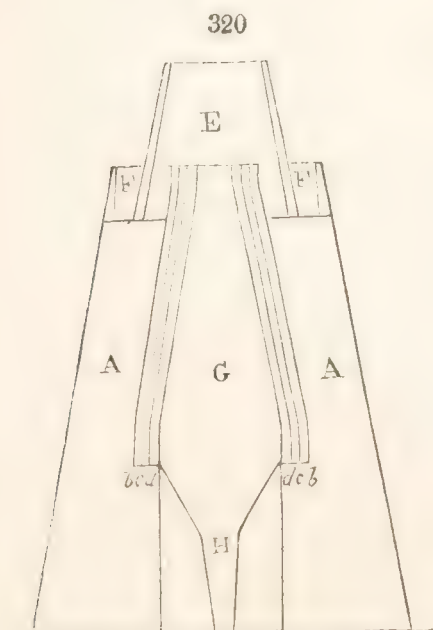
of the blast, and while it remains quiet at the bottom of the furnace, the globules of iron are precipitated from the slag, and occupy the lowest place, while the covering of scoriæ thus interposed between the metal and that portion of the blast which is reflected downwards, prevents it from suffering any further loss of carbon. In proportion as the melted matter accumulates, the slag, being the uppermost, flows out at the aperture made for this purpose: the iron is let out at regular intervals, into furrows made in sand, where it forms what is called *pig-iron*; or into a large reservoir, whence it is poured by means of ladles into moulds, forming all the various articles of *cast-iron* ware*.

* The following description and section of an iron smelting-furnace, is from the *Cabinet Cyclopædia*.

The exterior fabric of a blast furnace, or stack as it is called generally, resembles a truncated pyramid, constructed within of fire-proof materials, and without of brick or stone, according to circumstances. The shape of the internal orifice has been compared to a wine decanter placed upon a funnel, the greatest diameter of which is equal to the bottom of the decanter. The dimensions may be as follows:—The total height of the furnace fifty feet, the width of the top four feet diameter, the middle thirteen feet, the bottom two feet square, which is placed upon one end of a trough, six feet long, two deep, and two wide, called the hearth. The blast is introduced immediately above the hearth by a pipe of about two inches diameter on each side; of course before the metal on its extraction from the ore can descend into the hearth, it must pass the narrowest and hottest part of the furnace.

Figs. 320 and 321 represent a vertical section and the ground plan of a common coke blast furnace, reduced from the working plan of a practical builder.

AA, (fig. 320), the outer stack or building composed of Ashler stone or common brick.



bb, an inner casing of masonry, about fourteen inches thick, which, when the furnace requires to be renewed inside, admits of being taken down and rebuilt, without injury to the outer fabric.

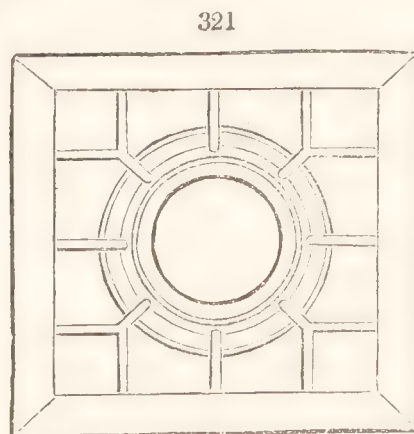
cc, a space of six inches filled with river sand, compactly rammed in: this medium being but an indifferent conductor of heat, tends to preserve the casing last described.

dd, a coating of the best fire bricks, fourteen inches in thickness.

E, a semicircular wall, eight or nine feet high, for the purpose of preventing the wind from blowing the flame upon the men or the machinery employed in serving the furnace.

FF, a lower wall, surrounding the one last mentioned, on the summit of those furnaces which are of old construction, as supplied by men from baskets, &c.

G, the inside of the furnace, for the reception of the materials during the process of fusion. The metal, as disengaged from the ore, descends by the pipe H into the hearth or receptacle in the centre of fig. 321, which is composed of similar materials with the superstructure.



The double lines converging from the sides, and carried through the outer circle in fig. 321, are simply open gutters left in the stonework by some builders, as vents for the escape of any small quantities of air which may be generated by what they term "the swelling of the furnace." These are not always inserted.

The following are some of the circumstances in the smelting which influence the quality of the produce. Much depends on the *fuel*: if the coke is not perfectly made, but retains bitumen, the whole mass cakes in the upper part of the furnace, and instead of descending regularly to the focus of heat, falls down at irregular intervals, so that part of the metal is detained too long before the blast, and decarbonized and oxidated, while other portions pass so rapidly through the furnace as never to be thoroughly reduced, hence the amount of the produce is diminished, and its quality deteriorated. Nor is it of less importance that the coke should be dry when put into the furnace. The *proportion of fuel* should also be adapted to the richness of the ore, so that there may be sufficient both to keep up the necessary degree of heat, as well as to carbonize the metal: hence, as the charges of ore and fuel are always proportioned by measure, if an ore somewhat richer than usual happens accidentally to be employed without a corresponding addition of fuel, the produce, though somewhat increased in quantity, will be more than equivalently reduced in quality. Another circumstance that the manufacturer must carefully attend to, is the proper choice of ore with regard to *fusibility*; for, as it is not only requisite that the iron should be melted, but also highly carbonized, and as coke gives off its carbon more difficultly than charcoal, a very fusible ore would melt long before it arrived at the focus of the furnace, and passing rapidly through, would reach the hearth without having had time to imbibe the proper quantity of carbon. Hence it is, that the rich *hæmatites*, although they afford an excellent quality of iron when smelted with charcoal, produce nothing but white iron when treated in the coke-furnace; while, on the other hand, *argillaceous ironstone* being much more refractory, does not melt till it comes into the very hottest part of the furnace, and therefore has had full time to absorb the desirable quantity of carbon.

Another thing to be attended to is the *proper regulation of the blast*, and this depends upon its dryness, its temperature, its compression, and its direction. The dryness and temperature appear to be principally governed by the season of the year. The dryer and colder the air is, the greater will be its effect on the combustion; and it is found that the produce of iron during the summer months, is inferior in quantity and quality to that which is manufactured in the winter: a clear, dry and severe frost is the most favorable period in every respect for the working of the furnace, and a change to snow or rain is followed by a corresponding deterioration. The higher the temperature of the blast when it is delivered into the furnace, the smaller will be the quantity of oxygen contained in every cubic foot, and, of course, the vigour of the combustion*. Nor is the force of the blast and its direction a subject of less

* Since this account of the manufacture of iron was written, an important change has been suggested in the introduction of the blast, in consequence of the discovery by Mr. Neilson, of Glasgow, of the saving of fuel and improvement in the iron, by sending a blast of *hot*, instead of cold, air, into the furnace. A notice of this discovery is given by Dr. Clark (*Edin. Phil.*

Trans., xiii.), of which the following is an abstract. The improvement consists in *heating* the air in its passage from the blowing machines to the furnace, and the following are the results of this system, obtained in the Clyde Iron-Works.

During the first six months of 1829, when all the cast-iron in the Clyde Iron-Works was made by the cold blast, a ton

importance; it is obvious, that in proportion as the charge descends, the carbonaceous matter is continually diminishing; hence the proper

of cast-iron required for fuel to reduce it, 8 tons $1\frac{1}{4}$ cwt. of coal, converted into coke. During the first six months of the following year, when the air was heated to near 300° Fahr., one ton of cast-iron required 5 tons $3\frac{1}{4}$ cwt. of coal, converted into coke. The saving amounts to 2 tons 18 cwt. on the making of one ton of cast-iron; but from that saving comes to be deducted the coals used in heating the air, which were nearly 8 cwt. The net saving thus was $2\frac{1}{2}$ tons of coal on a single ton of cast-iron. But during that year, 1830, the air was heated no higher than 300° Fahr. The great success, however, of those trials, encouraged the iron-masters to try the effect of a still higher temperature. Nor were their expectations disappointed. The saving of coal was greatly increased, so that, in 1831, Mr. Dixon, of Calder Iron-Works, attempted the substitution of raw coal for coke. The attempt was successful; and, since that period, the raw coal has been adopted in the majority of the Scotch iron-works. The temperature of the air under blast had now been raised so as to melt lead, and sometimes zinc, and therefore was above 600° Fahr., instead of being only 300° , as in the year 1830. It became, in consequence, so much elevated in temperature as to require the adoption of an old invention called the *water-tweezer*, which consists in surrounding the tuyere with water. The water is kept continually changing as it heats, by means of one pipe to admit the water cold, and another to let it escape when heated.

During the first six months of the year 1833, when all these changes had been fully brought into operation, one ton of cast-iron was made by means of 2 tons $5\frac{1}{4}$ cwt. of coal, (not previously converted into coke.) Adding to this, 8 cwt. of coal for heating, we have 2 tons $13\frac{1}{4}$ cwt. of coal required to make a ton of iron; whereas, in 1829, when the cold blast was in operation, 8 tons $1\frac{1}{4}$ cwt. of coals had to be used. This being almost exactly three times as much we have, from the change of the cold blast to the hot, combined with the use of coal instead of coke, *three times as much iron made from any given weight of splint coal*. The efficacy of a given quantity of air, in the production of iron, is also greatly increased, and the requisite proportion of flux diminished.

In regard to the *cause* of the above results, Dr. Clark observes, that it is necessary to discriminate between the quantity of fuel consumed, and the temperature produced. For instance, we may conceive a

stove at the temperature of 500° and lead put into it to melt. Then, since the melting-point of lead is more than 100° higher, it is evident that whatever fuel might be consumed in keeping that stove at 500° , is consumed to no purpose. In the manufacture of cast-iron likewise, a certain temperature is required to work the furnace favourably, and all the fuel consumed to produce any *lower* degree of temperature, is consumed in vain. How the hot blast increases the *temperature* of a furnace, will appear on adverting to the relative weights of the solid and gaseous materials used in the reduction of iron. As nearly as may be, a furnace, as wrought at Clyde Iron-Works, had two tons of solid materials an hour put in at the top, and this supply was continued for 23 hours a-day; one half-hour every morning and evening, being consumed in letting off the iron. But the gaseous material—the hot air—what might be the weight of it? This can easily be ascertained thus: I find, by comparing the quantities of air consumed at Clyde and at Calder Iron-Works, that one furnace requires of hot air from 2500 to 3000 cubical feet in a minute. I shall here assume 2867 cubical feet to be the quantity; a number that I adopt for the sake of simplicity, inasmuch as, calculated at an avoirdupois ounce and a quarter, which is the weight of a cubical foot of air at 50° Fahr., these feet correspond precisely with 2 cwt. of air a minute, or *six tons an hour*. Two tons of solid material an hour, put in at the top of the furnace, can scarce hurtfully affect the temperature of the furnace, at least in the hottest part of it, which must be far down, and where the iron, besides being reduced to metal, is melted, and the slag too produced. When the fuel put in at the top is coal, I have no doubt that, before it comes to this far-down part of the furnace, the place of its useful activity, the coal has been entirely coked; so that, in regard to the fuel, the new process differs from the old more in appearance than reality. But if two tons of solid material an hour, put in at the top, are not likely to affect the temperature of the hottest part of the furnace, can we say the same of six tons of air an hour, forced in at the bottom near that hottest part? The air supplied is intended, no doubt, and answers to support the combustion; but this beneficial effect is, in the case of the cold blast, incidentally counteracted by the cooling power of six tons of air an hour, or two cwt. a minute, which, when forced in at the ordinary temperature of the air, cannot be

situation for the focus of the blast is that part of the furnace, where, when the ore shall have arrived, it will be fully carbonized and surrounded with a sufficient quantity of fuel to excite an intense heat, and absorb nearly the whole of the oxygen of the air, and thus prevent it from either oxidating the iron, or carrying off the carbon with which it may be combined. This precise situation, in a furnace properly constructed, will be found to be just within the expansion of the boshes; but as this is more than four feet above the tuyere hole, the blast must be delivered with great velocity, and in a direction somewhat slanting upwards, in order that it may be reflected by the opposite wall of the crucible, and arrive at its proper place without undergoing any material decomposition. When the blast enters too rapidly, and in too concentrated a state, it renders the line of its passage, before it is reflected, so cool, that the descending slag which comes within its influence is suddenly solidified, and blown into a tube, reaching, perhaps, half-way across the crucible, through which the blast continues to rush; and in consequence of this protection, is conveyed with greater precision, and in a less decomposed state, into the upper part of the furnace. If, after this, the compression of the air is somewhat diminished, the tube still remains firm, often for days together, and the furnace works in the best manner. But, on the other hand, when too loose and soft a blast is admitted, and more especially if it is charged with moisture, it is unable to reach the top of the crucible without being decomposed, and the reflection which it undergoes from the wall of the crucible, weakens and disperses it to such a degree, that the combustion which ought to take place within the boshes, now occupies the whole upper part of the crucible: in consequence of this, the tube of scoriæ is presently burnt away, the iron almost as fast as it is melted, is ignited and oxidized, the tuyere-hole glows like the sun, with an intensely vivid white light; the scoriæ, from being yellowish-white streaked with blue, become green, brown, and finally black, nearly the whole of the iron in the state of oxide being taken up by it; the blocks of refractory grit-stone, with which the lower part of the furnace is lined, are worn into great holes, and in the space of a few hours prodigious damage is sustained. (AIKIN'S *Dictionary*, Art. IRON.)

VARIETIES OF IRON. An important part of the chemical history of iron relates to the varieties of the metal which are found in commerce. These are much too numerous to be dwelt upon here; so that we shall limit our observations to the principal of them only, which are *cast-iron*, *wrought-iron*, and *steel*.

CAST-IRON is essentially a *subcarburet*. There are two principal varieties of it, distinguished by the terms *white* and *grey*. *White cast-*

conceived otherwise than as a prodigious refrigeratory passing through the hottest part of the furnace, and repressing its temperature. The expedient of previously heating the blast obviously removes this refrigeratory, leaving the air to act in promoting combustion, without robbing the combustion of any portion of the heat it

produces. (See Dr. Clark's paper.) A short account of the contrivances for heating the air, with illustrative diagrams, and some useful memoranda upon the subject of cast-iron, are given in GRIER'S *Mechanic's Dictionary*. See also the *Encyclopædias*.

iron is very hard and brittle, and, when broken, of a radiated texture. Its composition approaches to Fe_4C . Acids act upon it but slowly, and exhibit a texture composed of a congeries of plates, aggregated in various positions. (DANIELL, *Quart. Journ. of Science and Arts*, vol. ii., p. 280.) *Grey* or *mottled iron* is softer and less brittle: it may be bored and turned in the lathe. When immersed in dilute hydrochloric acid, it affords a large quantity of black insoluble matter, which Daniell considers as a triple compound of carbon, iron, and silicium, and which has some very singular properties. The texture of the metal resembles bundles of minute needles. This variety of iron is occasionally substituted for wrought-iron, from its toughness and comparative purity; it sometimes contains only 3 or 4 *per cent.* of foreign matter. Beams, employed in building, and various parts of machinery, which formerly were exclusively made of wrought iron, are now frequently cast. When cast-iron is long submerged in sea-water, it often becomes converted into a substance much resembling graphite, a great part of the iron having been removed whilst the carbon remains: this change is especially observed in blocks of iron which have been attached to the copper sheathing of ships, with a view of preventing its corrosion (p. 224). Much information on the subject of the corrosion of iron by water is contained in a report by Mr. Mallet to the British Association (1839); he has also communicated a valuable paper on the subject to the Society of Civil Engineers.

A curious operation is often performed upon small articles made of cast-iron, in order to convert them into malleable iron, which is termed *decarbonization*, and is sometimes practised upon steel: it consists in bedding the articles in powdered oxide of iron (*hæmatite* is generally used), and exposing them to a red-heat: the carbon is thus abstracted from the cast-iron, and it becomes as flexible and malleable as wrought-iron.

The following are the analyses of three samples of the best grey cast-iron, from the furnaces of South Wales, by Gay Lussac.

	I.		II.		III.
Carbon	2·450	2·550	1·666
Silicium.....	1·620	1·200	3·000
Phosphorus	0·780	0·440	0·492
Manganese	a trace	a trace	a trace
Iron	95·150	95·810	94·842
	<hr/>		<hr/>		<hr/>
	100·000		100·000		100·000

In some foreign cast-iron the proportion of manganese is much more considerable, amounting to from 2 to 5 *per cent.* It will be obvious, by a reference to the composition of steel, that if the process of decarbonization be not carried to its full extent, cast-iron may thus be converted into steel; and what is termed *natural steel* is in fact steel so obtained.

WROUGHT-IRON. Cast-iron, after it has been to a certain extent *refined*, by fusion in a forge, in contact with charcoal, is in this country converted into wrought-iron by a curious process, called *puddling*. The cast-iron is put into a reverberatory furnace, and when in fusion is stirred, so that every part may be exposed to the air and flame. After a time

the mass heaves, emits a blue flame, and gradually grows tough, and becomes less fusible, and at length pulverulent; the fire is then urged, so that the particles again agglutinate at a welding heat, and are gradually wrought up into masses. In that state of intense heat the masses are passed successively between rollers, by which a large quantity of extraneous matter is squeezed out, consisting chiefly of fusible carburet of iron and slag, and the iron becomes malleable. The bars, into which it is formed, are cut into pieces, placed in parcels in a very hot reverberatory furnace, and again hammered, or rolled out into bars. They are thus rendered more tough, flexible, and malleable, but much less fusible, and may be considered as nearly *pure iron*.

The process of puddling has lately been improved by adding oxide of iron, or of manganese, to the mass of iron, so as to assist in burning out the carbon. Cast iron may be represented as a carburet, composed nearly of 4 atoms of iron ($28 \times 4 = 112$, and 1 of carbon $= 6$; "thus, by heating together 2 parts of cast-iron and 1 of the scales of black oxide of iron from a forge, all the carbon and oxygen pass off as carbonic acid, and the iron of both remains pure. Fe_3O_4 and Fe_8C_2 produce Fe_{11} and 2CO_2 ." (KANE.)

STEEL. This extraordinary and valuable substance is a compound of iron with a small relative proportion of carbon*, which varies in the varieties of steel. Other substances are also occasionally present, which apparently modify some of its characters: traces of phosphorus, sulphur, and manganese, are not uncommon. It combines the fusibility of cast with the malleability of bar-iron, and when heated and suddenly cooled it becomes very *hard*, but may again be softened by the careful management of heat; hence its superiority for the manufacture of cutting instruments, and an almost infinite number of useful purposes in the arts. If kept for a long time in fusion, it loses carbon and becomes pure iron. Its texture, when examined by the action of an acid, is not fibrous, but lamellated.

Steel may be formed from the native oxides of iron, or from the purer varieties of cast-iron, by so modifying the process of reduction as to leave the iron in combination with no more carbon than is requisite, and in that case it has sometimes been termed *native steel*. Iron may also be con-

* The identity of charcoal and diamond above adverted to, receives additional proof by the conversion of iron into steel when that metal is ignited with diamond powder. Upon this subject some controversy will be found in the *Phil. Mag.*, vol. v.; the *experimentum crucis* is, however, due to Pepys, who availed himself of Children's Voltaic battery of large plates for the production of the requisite heat (*Phil. Trans.*, 1815, p. 371): he bent a wire of pure soft iron so as to form an angle in the middle, in which part he divided it longitudinally by a fine saw; in the opening so formed he placed diamond-powder, securing it in its situation by two finer wires, laid above and below it, and kept from

shifting by another small wire, bound firmly and closely round them. All the wires were of pure soft iron, and the part containing the diamond-powder was enveloped by thin leaves of talc. Thus arranged, the apparatus was placed in the electrical circuit, where it was kept red-hot for six minutes: on opening the wire the diamond had disappeared, the interior surface of the iron had fused into numerous cavities, notwithstanding the very moderate heat to which it had been exposed, and all that part which had been in contact with the diamond was converted into perfect blistered-steel. A portion of it being heated red and plunged into water, became so hard as to resist the file and to scratch glass.

verted into steel by passing carburetted hydrogen over the bars at a high red heat. (MACINTOSH.) But steel is generally made by a process called *cementation*, which consists in heating bars of the *purest* iron in contact with charcoal; it absorbs carbon, and increases, according to Mushet, in weight*, at the same time acquiring a *blistered* surface. That carbon is vaporizable, and that it may enter into and combine with the iron in the form of vapor, appears probable from the experiments of Le Play and Laurent (*Ann. Ch. et Ph.*, LXV. 417); yet it is sometimes doubted how far any carbon is actually absorbed in the common process of steel-making, for we never find wrought-iron absolutely free from carbon, and sometimes it seems rather to lose than gain it; perhaps, therefore, some more intimate union between the carbon and iron is effected by cementation, for it is scarcely possible that a mere change in the mechanical texture of the iron can give it the properties of steel, and Pepys's experiment with iron and diamond, referred to in the note to the preceding paragraph, is in favor of actual carbonization. It is sometimes supposed that in the process of steel-making the carbon is presented to the iron in the form of carbonic oxide, which, penetrating into the pores of the heated bar, is decomposed into carbon and carbonic acid, ($2\text{CO}=\text{CO}_2$ and C,) and that the escape of the latter causes the blistered appearance.

When blistered-steel is drawn down into smaller bars and beaten, it forms *tilted-steel*; and this broken up, heated, welded, and again drawn out into bars, forms *shear-steel*. *English cast-steel* is prepared by fusing blistered steel with a flux composed of carbonaceous and vitrifiable ingredients, casting it into ingots, and afterwards, by gentle heating and careful hammering, or rolling, giving it the form of bars.

By comparing the analysis of blistered-steel with that of cast-steel, it would appear that in the intense heat to which the metal is necessarily subjected for its fusion, it loses silicium and a little carbon; but the great superiority of cast-steel for many of the purposes of the arts, no doubt depends upon its comparative uniformity of composition. The following are analyses of three samples of blistered-steel by Vauquelin, and four of cast-steel by Gay Lussac.

	Blistered-Steel.				Cast-Steel.								
Carbon	0·79	...	0·68	...	0·63	...	0·62	...	0·65	...	0·65	...	0·94
Silicium.....	0·15	...	0·12	...	0·11	...	0·03	...	0·00	...	0·04	...	0·08
Phosphorus ...	0·34	...	0·82	...	1·52	...	0·03	...	0·08	...	0·07	...	0·11
Iron	98·72	...	98·38	...	97·74	...	99·32	...	99·27	...	99·24	...	98·87
	<hr/> 100·00		<hr/> 100·00		<hr/> 100·00		<hr/> 100·00		<hr/> 100·00		<hr/> 100·00		<hr/> 100·00

It appears probable that the proportion of carbon in the above analyses must be somewhat underrated: the first column of Gay Lussac's table

* The following table by Mushet, shows the quantities of charcoal which disappeared during the conversion of iron into the different *subcarburets of iron* known in commerce. (*Phil. Mag.*, xiii.)

When the carbon amounts to $\frac{1}{60}$ of the whole mass, the hardness is at a maximum.

Charcoal absorbed.

RESULTS.

$\frac{1}{120}$ - - - soft cast-steel.

$\frac{1}{100}$ - - - common cast-steel.

$\frac{1}{95}$ - - - the same but harder.

$\frac{1}{50}$ - - - the same, too hard for drawing.

$\frac{1}{25}$ - - - white cast-iron.

$\frac{1}{20}$ - - - mottled cast-iron.

$\frac{1}{15}$ - - - black cast-iron.

gives the components of the best English cast-steel, and the two last that of French steel of first and second quality. My experience in the use of steel for the manufacture of dies for coinage has been considerable, and the denomination of steel which we prefer for that purpose at the Mint, approximates, as far as the few specimens which I have examined enable me to infer, to the composition given in the last column; at least, when the carbon has fallen short of 1 *per cent.* I have found it deficient in hardness, and when it has exceeded 1 *per cent.* the dies have split under the multiplying press, or if hardened, have not stood to their work in the coining presses. But the quality of steel is doubtless much influenced by minute proportions of other bodies. and unless it contains a sensible quantity of phosphorus it cannot be depended upon for the manufacture of dies, though I have not been able to satisfy myself of the exact requisite relative proportion. Much, also, must depend upon mere *mechanical* differences. The trials to which steel is subjected, under the form of coining-dies, are extremely rigorous, and its mechanical as well as its chemical characters greatly influence its fitness for the purpose; but it would occupy too much space here to enter into detail upon these matters, which are in a great measure foreign to our present subject.

WOOTZ, or INDIAN STEEL, which has, by some, been considered as superior to any other for the purpose of making certain edge-tools, apparently derives its peculiar excellence from combination with a minute portion of aluminum and silicium. (*Quart. Journ. of Science*, vii. 288.) Whether these substances are in the ore, or are furnished by the crucible used in making the steel, is not certainly known. Wootz, in the state in which it is imported, is not fit to make into fine cutlery; it requires a second fusion, by which the whole mass is purified and equalized, and fitted for forming the finest edge-instruments.

CASE-HARDENING is an operation performed upon cast or wrought-iron, by which it is superficially converted into steel: the article is for this purpose either heated to redness in a crucible, or vessel containing charcoal powder; or sometimes, if small and delicate, is wrapped round with leather, and then gradually heated to redness, and kept in that state till its surface is duly carbonized. Ferrocyanide of potassium is also a valuable material as a case-hardener, and in various operations connected with the management of steel.

HARDENING AND TEMPERING STEEL. When steel is heated to a cherry-red color, and then plunged into cold water, it becomes so extremely hard and brittle, as to be unfit for almost any practical purpose. To reduce it from its extreme hardness, is called by the workmen *tempering*, and is effected by again heating the steel to a certain point. The surface being a little brightened, exhibits, when heated, various colors, depending upon the formation of thin films of oxide*, which constantly

* That the color produced on the surface of heated steel is the effect of oxidation, is proved from the circumstance that when steel is heated and suffered to cool under

mercury or oil, none of the colors appear: nor do they when it is heated in hydrogen or nitrogen.

change as the temperature is increased, and by these colors it has been customary to judge of the temper of the steel. But a more accurate, as well as convenient method, is to use a bath and thermometer; the bath may be of mercury, or of the fusible mixture of lead, tin, and bismuth, or, indeed, of any fluid whose boiling-point is not much under 600° . Into this bath the articles to be tempered are put, together with the bulb of a thermometer graduated to the boiling-point of mercury. The corresponding *degrees* at which the various colors appear are from 430° to 600° . The first change is at about 430° , but this is too faint to be distinguished, except by comparison with another piece of untempered polished steel. At 460° the color is *straw*, becoming deeper as the temperature is increased; at 500° the color is *brown*; this is followed by a *red* tinge with streaks of *purple*, then *purple*, and at nearly 600° it is *blue*. The *degrees* at which the respective colors are produced being thus known, it follows that the workman has only to heat the bath, with its contents, up to the required point. For example, suppose the blade of a penknife (or one hundred of them) to require tempering: they are suffered to remain in the bath until the mercury in the thermometer rises to 460° , and no longer, that being the heat at which the knife (supposing it to be made of the best English cast-steel) will be sufficiently tempered. The advantages attending this method are obvious; the heat is equally applied to the whole; and the workman, instead of attending to the color of each blade, has only to observe the thermometer.

It has been found that steel, for certain uses, is sufficiently tempered long before it is heated to produce any change of color, a circumstance which gives additional value to the process by a thermometer. The knife-edges attached to a pendulum described by Capt. Kater (*Phil. Trans.*, 1818, p. 38), were forged by Mr. Stodart, from a piece of fine wootz. They were carefully hardened, and tempered in the bath at 430° ; on trial they were found too soft. They were a second time hardened, and then heated to 212° . The intention was to increase the heat from that point, trying the temper at the advance of about every ten degrees. In the present instance this was not necessary, the heat of boiling water proving to be the exact point at which the knife-edges were admirably tempered. It is highly probable that steel, for many uses, may be sufficiently tempered in a range so extensive as from 212° to 430° , and, by the thermometer, all the intervening degrees may be certainly ascertained. But it is not the temperature only, but also the time during which the steel is exposed to it, which influences its hardness or temper.

What may be the changes effected in the molecular constitution of steel by the operation of hardening is an important, but a very difficult and undecided question; that they are considerable, there can be no doubt, but that they extend beyond mechanical arrangement, and affect chemical composition, according to the notions of Karsten, is a theory which requires much more satisfactory proof than it has hitherto received; nor are the changes which other substances undergo by a similar operation in any way illustrative of or applicable to those of steel, the electromagnetic properties of which are not less remarkable than the coarser mechanical changes which it sustains, and which are in all probability someway related to each other, and to the more abstruse causes of crystal-

line peculiarities. There is certainly in many points an analogy between unannealed or suddenly cooled glass and tempered or hardened steel, and the extraordinary molecular and crystalline peculiarities of glass, when more correctly understood, may perhaps tend to throw some light upon the more obscure subject of steel, but as yet this is not the case. It is, however, by no means uncommon to find the same unstable arrangement of particles and inequality of tension in a mass of hardened steel, as in a lump of glass which has solidified in cold water; from the surface to the interior, successive crusts or coats of variable texture and hardness present themselves. Sometimes a steel die, after it has been for some time hardened and apparently safe, will split with an audible report, and its fracture then exhibits a soft core covered by successive coats or layers, increasing in hardness from the centre towards the exterior.

In addition to the difficulties arising out of the mass with which he has to deal, and the changes of texture, if not of composition, which it has necessarily been subjected to in the various operations of perfecting the impression from the punch in the press, the manufacturer of dies for medals or coinage has another obstacle to contend with, which is the necessity of keeping the face or work of the die perfectly clean and free from scales and oxidizement, so that it may not only be without any obvious blemish, but present that peculiar velvety hue which so much enhances the beauty of the subsequent impressions in gold, silver, or copper: to this end the charcoal in which the die is imbedded, when it is heated previous to hardening, must be carefully looked to; it should be animal charcoal, and cyanogen, if present, is rather favourable than otherwise to the ultimate result; moisture, air, potassium, sulphur, and other things sometimes present in charcoal, are injurious; and when the die is at a proper heat and ready to be plunged into the hardening cistern, or submitted to the sudden action of a gush of water, all contact of air with the face of the die must be scrupulously avoided. Protecting pastes are seldom of much use.

The degree of hardness attainable by steel will depend upon the heat to which it had been raised, and the coldness of the water or other medium into which it is plunged; so that when very cold water cannot be procured, the die or other article must be heated proportionately high; a dull red heat into water at 34° , a cherry red into water at 50° , an orange heat into water at 80° , and a dull white heat into water at 100° , produce nearly the same effects; but the real hardness attained in water which is warm never equals that given by cold water: a red heat and water at 45° is the most desirable for die hardening: and although by subsequent tempering the die may, if necessary, be *brought down*, or softened, it is always safest to give it, if possible, its due hardness by the first operation. The risk of injuring the face of a die by oxidizement or scaling, or of *burning* the die, as it is usually called, increases greatly with a high temperature, and this is another reason why, in this particular branch, a moderate heat and very cold water is greatly to be preferred to a higher heat and warmer water. The hardening of steel when in thin bars, or other regular form, and where extreme cleanliness of surface is dispensed with, is comparatively an easy and certain operation.

The aspect of steel when so broken as to exhibit a clean fracture,

varies from an uniform silky and even surface of an almost silvery whiteness, to a fine or even coarse-grained texture, of a more blue or iron-like aspect; the finer-grained varieties are generally preferred, but no very important or at least unerring conclusions respecting its quality can be drawn either from texture or color. The microscope, however, enables us to observe some remarkable peculiarities in steel, not only in its varying texture as it comes from the manufacturer, but also before and after hardening. The fact of its diminution of density after hardening, or in other words, the increase of bulk which it then sustains, has long been known. Steel, of the specific gravity of 7.738, was found by Hawksbee to be thus reduced to 7.704. Brisson found the density of good English steel to be increased by hammering from 7.833 to 7.872. After hardening, the former had decreased to 7.816, and the latter to 7.818. Dr. Thomson found the density of good blistered-steel to be 7.823; when heated to redness and suddenly plunged into cold water its density was reduced to 7.747. The specific gravity of a piece of cast-steel he found = 7.8227; but when hardened only = 7.7532; (*Inorg. Chem.*, i. 497.) I have found even greater differences; and, in fact, the higher the heat to which the steel is raised, and the colder the medium in which it is cooled, the greater will be the resulting difference of density; for it is probable that the increased bulk attained by the steel under the expansive influence of heat, is retained by the suddenly cooled mass, and hence the peculiar state of tension into which it must be thrown when it has ultimately cooled down to the temperature of the atmosphere; and, indeed, it is surprising that masses of steel, which have undergone the process of hardening, are not more brittle and uncertain than experience proves them to be. According to Regnault, the mean specific heat of soft steel is 0.1165: that of hardened steel 0.1175. (*Ann. Ch. et Ph.*, Nov. 1843, p. 343.)

The quality of steel is sometimes tested by washing over its clean surface with dilute nitric acid, which ought to produce an uniform grey or blackish color: if the steel is imperfect, and contains veins or pins of iron, they become evident by their difference of color. When some particular kinds of iron or steel are thus tested, a mottled appearance is produced, as if it were composed of layers or wires of iron and steel welded together: hence is supposed to arise the peculiar character of the celebrated *Damascus* sword-blades.

ALLOYS OF STEEL. Attempts have been made to improve the quality of steel by alloying it with some other metals, but none of these combinations have been found, after due experience, to be superior to the best ordinary steel. We shall again have occasion to notice them; but for details upon this subject, the reader is referred to the papers of Messrs. Stodart and Faraday, already quoted (*Quart. Journ.*, ix. 319, *Phil. Trans.*, cxii. 253), and to the volume of LARDNER'S *Cyclopædia*, treating on iron and steel.

§ X. ZINC. Zn. 32.

ZINC, or *Spelter*, as it is sometimes called in commerce, is found in the state of oxide and of sulphuret. The metal zinc is first mentioned by Paracelsus, but the use of its ores, in converting copper into brass, was probably known to the ancients. In China and India zinc is said to have been known from time immemorial, and various utensils of zinc, sometimes inlaid and ornamented with other metals, are common in those countries. Perfectly pure zinc is difficultly obtained; it may be procured in a state approaching to extreme purity by dissolving the purest kinds of zinc that occur in commerce in dilute sulphuric acid, and immersing a plate of zinc for some hours in the solution, which is then filtered, decomposed by carbonate of potassa, and the precipitate, after having been welledulcorated, heated with charcoal in an iron or earthen retort in a proper furnace. The zinc being volatile at a white-heat may thus be distilled over into water, care being taken that the neck of the retort is short and wide, otherwise it will be stopped up by the condensed metal. The common zinc of commerce may contain traces of lead, copper, iron, cadmium, arsenic, sulphur, manganese, and carbon: its impurities are the source of a black powder which remains when it is dissolved in dilute sulphuric acid; but arsenic (and probably minute portions of other metals) may be carried off with the hydrogen. The following are analyses of 3 samples of Austrian zinc by Wittstein, and of a sample of commercial zinc by Jacquelain.

Zinc	96·27	99·05	98·76	99·170
Lead	3·33	0·27	0·91	0·685
Cadmium	0·30	0·23	0·16	—
Iron	0·10	trace	0·17	0·142
Carbon	—	—	—	0·003
	<hr/>		<hr/>		<hr/>		<hr/>
	100·00		99·55		100·00		100·000

Pure zinc, when dissolved in pure sulphuric acid, should evolve perfectly pure hydrogen and leave no residue: the acid solution should give no precipitate with sulphuretted hydrogen, neither should it occasion any deposit upon a plate of immersed zinc: the precipitate produced in this solution by potassa should be perfectly soluble in excess of the alkali: the solution of pure zinc in nitrohydrochloric acid should give no precipitate with solution of chloride of barium. (GMELIN.)

Zinc is a bluish-white metal, with considerable lustre, rather hard, of a specific gravity of about 6·8 in its usual state, but, when drawn into wire, or rolled into plates, its density is augmented to 7 or 7·2. Its specific heat is 0·09555. (REGNAULT.) It has a peculiar odor when breathed upon or handled with moist fingers. In its ordinary state, at common temperatures, it is tough, and with difficulty broken by blows of the hammer. It becomes very brittle when its temperature approaches that of fusion, which is about 773°, (DANIELL); but a temperature a little above 212°, and between that and 300°, it becomes ductile and malleable, and may be rolled into thin leaves, and drawn into moderately fine wire, which, however, possesses but little tenacity. When a mass of zinc, which has been fused, is slowly cooled, its fracture exhibits a lamellar and prismatic crystalline texture. The equivalent of zinc is 32. (32·2

GMELIN: 32.26 BERZELIUS: 32.3 TURNER: 32.31 GRAHAM: 33.12 JACQUE-LAIN.)

When a surface of clean and polished zinc, which may be made beautifully brilliant, is exposed to dry air, it remains bright at common temperatures; in damp air it soon tarnishes, and acquires a grey color from a film of superficial oxide: it then remains for a long time unchanged. A plate of zinc placed under a bell-glass containing air free from carbonic acid, and standing over water, becomes bedewed and superficially oxidized; but if a piece of tarnished lead be under the same bell-glass, but not in contact of the zinc, drops of water collect upon the lead only, and the zinc remains clean. Whenever two metals not in contact are treated in this way, the most oxidizable is only bedewed and consequently oxidized; this is the case with arsenic or lead, near copper or silver, but the latter metals when alone under the bell-glass are bedewed: when on the other hand, the metals *are in contact* then the least oxidizable metal is only bedewed: thus when copper is in contact of zinc, the copper only is bedewed, and when copper is in contact of silver, the silver only is bedewed. (BONSDORFF, *Poggend.*, xlii. 325.) Under water free from carbonic acid zinc becomes enfilmed with hydrated oxide, or with a hydrated basic carbonate if carbonic acid be present. At common temperatures zinc does not decompose pure water, but it does so at a red-heat, or in the presence of acids. In pure water, from which air is carefully excluded, zinc remains bright.

It has been ascertained by A. de la Rive, that the energy with which zinc is acted on by dilute sulphuric acid is greatly dependent upon the purity of the metal; that when perfectly pure the action is comparatively feeble, but that when it contains minute portions of other metals, not exceeding (in regard to iron) a 100th to 200th part, the action becomes rapid: this is apparently owing to galvanic causes (see p. 224); and when a piece of pure zinc is wound round with platinum wire an equivalent effect is produced. De la Rive examined the action of dilute sulphuric acid on pure zinc, and on alloys of 9 parts of pure zinc with 1 of the several metals which are usually found in it, with the following results:—

	Gas evolved in a given time.
Zinc of commerce, and alloy of zinc and iron	100
Alloy of zinc and copper	43
„ zinc and lead	15
„ zinc and tin	12
Distilled zinc	5

A mixture of 100 parts of water with from 33 to 50 of sulphuric acid is that which acts most intensely on the metal.

Zinc has lately, in consequence of its lightness and cheapness, been much used for roofing, gutters, and chimney-tops; but it should not, as is sometimes the case, be rivetted with copper nails, the contact of which with the zinc accelerates the decay of the latter by electric action: indeed any of the common metals in metallic contact with zinc, tend to the oxidizement of the latter.

ZINC AND OXYGEN. The high attraction which exists between zinc and oxygen, is shown by the facility with which nearly all the other metallic oxides, when in solution, are reduced to the metallic state by its

means. Its important electro-generative power in the Voltaic apparatus, is also referable to this cause. By exposing zinc to the joint action of heat and air at a temperature just sufficient to fuse it, it is converted into a grey powder, which is probably a mere mixture of metallic zinc and oxide of zinc: though by some it is regarded as a true *suboxide*, Zn_2O . A similar compound is obtained, according to Dulong, by decomposing oxalate of zinc at a red-heat in a retort.

PROTOXIDE OF ZINC. ZnO . This is the only salifiable oxide of zinc: it is obtained, 1. by intensely heating the metal exposed to air, when its vapor takes fire, and air being freely admitted, burns with a very bright flame, and forms a white flocculent tasteless substance, formerly called *nihil album*, *philosopher's wool*, and *flowers of zinc*. When this combustion goes on with violence, the oxide, though in itself not volatile, is carried up in flocculi by the current of air, which are so light as to remain for a long time floating about in the atmosphere. If the large flakes of oxide which collect in the mouth of the crucible when zinc is thus burned, be carried into a dark room, they have been observed to remain for a long time phosphorescent. A piece of rolled zinc-leaf may also be inflamed by a spirit-lamp, and will continue to burn brilliantly even when removed from the flame: if inflamed and plunged into a jar of oxygen gas, the combustion is as vivid as that of phosphorus; indeed the splendor of the flame probably arises in both instances from the same cause, namely, the ignition of finely-divided solid incombustible matter (p. 127.) The oxide of zinc, as prepared by combustion, generally contains small particles of the metal, which render it gritty, and require to be separated by washing; it may also contain various impurities derived from the metal, so that for pharmaceutical use it is best prepared by the next process. 2. A solution of pure sulphate of zinc is decomposed at a boiling heat by its equivalent of carbonate of soda; the precipitate well washed, dried, and exposed to a dull red-heat, is a pure oxide: or the cold solution of the sulphate may be decomposed by carbonate of ammonia, and the precipitate washed and dried as before. Traces of sulphuric acid, or of soda, may generally be detected in the oxide from cold solutions where carbonate of soda is used, and if a hot solution be precipitated by carbonate of ammonia, the oxide always retains sulphuric acid. Gmelin observes that the purest oxide would be obtained by precipitating pure nitrate of zinc by carbonate of ammonia, and heating the precipitate to redness.

Oxide of zinc obtained by the combustion of the metal, or by passing steam over red-hot zinc, is sometimes crystalline: its sp. gr. is between 5.6 and 5.7. It is commonly met with in the form of white powder: at a high temperature it acquires a yellow tint, but again whitens as it cools. It has been used as a pigment, both with oil and water, and is employed in medicine as a tonic, and as an external application. When made upon a large scale from common zinc, it is tainted by oxide of iron and other substances: the whiter parts of such oxide used to be called *pompholix*, and the grey, or less pure portions, *tutty*. A patent has been taken for the employment of these and other impure oxides of zinc, as a substitute for white lead in the manufacture of common oil paint, it appearing that they are equally capable of combining with, or producing a *body* as it is termed, when ground with linseed or other drying oil.

Oxide of zinc is readily soluble in the acids; it also dissolves, especially in the state of hydrate, in the caustic fixed alkalis, and in pure and carbonated ammonia. The strong ammoniacal solution becomes turbid when dilute, and deposits its oxide when boiled. The solutions in potassa and soda yield a white deliquescent mass on evaporation: these, however, can scarcely be called chemical combinations. When a solution of alumina in caustic potassa is mixed with an ammoniacal solution of oxide of zinc, a definite combination of the earth and oxide is thrown down, containing, according to Berzelius, 6 atoms of alumina and 1 of oxide of zinc, and being identical in composition with the mineral called *Gahnite*.

Protoxide of zinc consists of

					Proust.	Berzelius.	Gay Lussac.	Döbereiner.	
Zinc	1	...	32	...	80	...	80·1	...	81·64
Oxygen	1	...	8	...	20	...	19·9	...	18·36
<hr/>									
Protoxide of zinc	1		40	100	100		100·0	100·00	100·00

The commercial oxide of zinc is sometimes adulterated with starch, chalk, carbonate of magnesia, or alumina. Starch is detected by iodine; alumina may be separated by acetic acid, which dissolves the oxide of zinc; when the solution has been precipitated by a hydrosulphuret, lime and magnesia may be detected by the usual tests. In medicine, oxide of zinc is employed as a tonic, but by long-continued use it acts as a slow poison. (PEREIRA. *Mat. Med.*)

Hydrated oxide of zinc. ZnO, HO , may be obtained in crystals, (SCHINDLER, *Mag. der Pharm.*, xxxi.) by the action of ammonia upon zinc in contact of iron; hydrogen is evolved, and in the course of eight days rhombic prisms of hydrated oxide of zinc are deposited. When nitrate of zinc is precipitated by potassa not in excess, a white bulky hydrate falls. It consists of

						Schindler.
Oxide of zinc.....	1	...	40	...	81·63 81·62
Water	1	...	9	...	18·37 18·36
<hr/>						
Hydrated oxide of zinc....	1		49		100·00	100·00

Thenard has described a *peroxide of zinc* obtained by the action of peroxide of hydrogen on hydrated oxide of zinc, which unless kept at 32° , evolves oxygen. (*Ann. Ch. et Ph.*, ix. 55.)

CHLORIDE OF ZINC. ZnCl , is formed, 1. By heating leaf-zinc in chlorine: very thin leaves burn in the gas, and if chlorine be passed over zinc heated nearly to its point of fusion, the combination takes place with ignition. 2. By evaporating a solution of zinc in hydrochloric acid to dryness, and heating the residue red-hot in a glass tube with a small aperture; or the evaporated chloride may be distilled over at a red-heat. 3. By distilling a mixture of 1 part of zinc filings and 2 of corrosive sublimate; or a mixture of dried sulphate of zinc and chloride of sodium. It is a white semi-transparent substance, extremely deliquescent, fusible at 300° , and volatile at a bright red-heat: its vapor condenses in acicular crystals; it forms combinations with sal-ammoniac and with chloride of potassium. It has a nauseous styptic taste, and is powerfully emetic.

It is used in surgery as a caustic, and in medicine, in very minute doses, as a tonic. It was formerly called *butter of zinc*. It is readily soluble in water, and the solution gives on evaporation a very difficultly crystallizable and deliquescent hydrate generally called *muriate of zinc*, ($\text{ZnCl}_2 \cdot \text{HO}$) which, when heated in the open air, partly sublimes in the form of chloride, and is partly resolved into hydrochloric acid and oxide of zinc, in consequence of the decomposition of water. Its concentrated solution deposits oxide of zinc upon the addition of water, and the diluted solution dissolves the oxide when concentrated by evaporation. The solution of chloride of zinc is always slightly acid, and the addition of ammonia does not render it neutral till all the oxide is precipitated. The attraction of zinc for chlorine is so great, that it is often employed for separating chlorine from other combinations. Sir William Burnett's preservative against dry rot is a dilute solution of chloride of zinc, and it is very effectual. Chloride of zinc consists of

						J. Davy.
Zinc.....	1	32	47 50
Chlorine	1	36	53 50
<hr/>						<hr/>
Chloride of zinc	1		68		100	100

OXICHLORIDES OF ZINC. Chloride of zinc combines with oxide of zinc in several proportions: three of these have been particularly examined. 1. $\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 4\text{HO}$, formed by boiling oxide of zinc in a strong solution of the chloride; or by decomposing chloride of zinc by a small quantity of ammonia, and boiling the precipitate in the liquor. By the first process it yields small octohedra; by the second it is a white powder, sparingly soluble in water, more so in solution of the chloride, and readily soluble in acids, and in caustic ammonia and potassa. (SCHINDLER.) 2. $\text{ZnCl}_2 \cdot 6\text{ZnO} \cdot 10\text{HO}$, formed by the action of water upon ammonio-chloride of zinc. (KANE.) 3. $\text{ZnCl}_2 \cdot 9\text{ZnO} \cdot 14\text{HO}$, formed by adding potassa to solution of chloride of zinc till the alkali begins to predominate. (KANE.) The proportions of water in these compounds vary with the temperature at which they are dried.

AMMONIO-CHLORIDES OF ZINC. Several of these have been examined by Dr. Kane. 1. $2\text{NH}_3 \cdot \text{ZnCl}_2 \cdot \text{HO}$, obtained by passing gaseous ammonia through a hot concentrated solution of chloride of zinc till the precipitate redissolves: then filtering and setting aside to crystallize. 2. $2[\text{NH}_3\text{ZnCl}] + \text{HO}$, obtained from the mother-liquor of the preceding. 3. $\text{NH}_3 \cdot 2\text{ZnCl}_2$ is formed by the fusion of either of the preceding salts. According to Pierre (*Ann. Ch. et Ph.*, Fevr. 1846) a double chloride of zinc and ammonium is easily obtained by dissolving 1 equivalent of chloride of zinc and 1 of sal-ammoniac in water, and crystallizing: it forms oblique prisms, slightly deliquescent, and very soluble $= \text{ZnCl}_2 \cdot \text{NH}_4\text{Cl}$.

POTASSIO-CHLORIDE OF ZINC. $\text{ZnCl}_2 \cdot \text{KCl}$, is a very soluble salt obtained by evaporating the mixed solution of 1 equivalent of each of its component chlorides: it forms small lamellar deliquescent crystals, which are anhydrous, and fuse at about 390° . At a dull red-heat they evolve vapor of chloride of zinc. (PIERRE.)

CHLORATE OF ZINC. ZnO,ClO_5 , crystallizes in octohedra, and is a very soluble salt. It is obtained by dissolving carbonate of zinc in chloric acid. When metallic zinc is digested in chloric acid, a portion of chloride of zinc is formed. (VAUQUELIN, *Ann. de Ch.*, xcv. 116.) Obtained by decomposing chlorate of baryta by sulphate of zinc, and evaporating over sulphuric acid in vacuo, it affords a deliquescent crystalline mass ($\text{ZnO},\text{ClO}_5,6\text{HO}$) soluble in alcohol, fusing at 140° , and at a higher temperature losing chlorine, oxygen, and water, and leaving oxide of zinc.

PERCHLORATE OF ZINC. ZnO,ClO_7 , formed by precipitating perchlorate of baryta by sulphate of zinc, yields small deliquescent crystals soluble in alcohol. (SERULLAS. *Ann. Ch. et Ph.*, xLvi. 305.)

IODIDE OF ZINC. ZnI . Iodine and zinc exert a powerful mutual affinity: the iodide is easily obtained by adding iodine to zinc filings in water, and applying a gentle heat: the iodine is added till it begins to discolor the solution; in excess, it is dissolved by the iodide which is formed. On evaporating the solution to dryness in a retort, the remaining iodide of zinc may be fused, and at a higher temperature it rises in vapor, and condenses in prismatic crystals. Heated in the open air, iodine goes off, and oxide of zinc is formed: its aqueous solution is also decomposed by exposure to air, with the separation of iodine and the formation of oxide. It consists of

						Gay Lussac.	Rammelsberg.
Zinc	1	...	32	...	20.4	20.48	20.347
Iodine.....	1	...	126	...	79.6	79.52	79.653
<hr/>							
Iodide of zinc.....	1		158		100.0	100.00	100.000

IODIDE OF ZINC AND SODIUM yields on spontaneous evaporation, acicular crystals very soluble and deliquescent, $=\text{NaI},\text{ZnI}$.

IODATE OF ZINC. ZnO,IO_5 . When a soluble iodate is added to a solution of sulphate of zinc, it forms a difficultly-soluble iodate of zinc, which gradually falls in spheroidical grains. The salt may also be formed by dissolving recently precipitated oxide or carbonate of zinc in iodic acid. (GAY LUSSAC, *Ann. de Chim.*, xci. 85.) It dissolves in 114 of water at 60° , and in 76 at 212° . The formula of the crystals is $\text{ZnO},\text{IO}_5,2\text{HO}$. (RAMMELSBERG.)

BROMIDE OF ZINC. ZnBr , is formed by passing bromine vapor over heated zinc; the mutual action of bromine and zinc is not very intense. Bromide of zinc has a sweetish astringent taste; is very deliquescent; fuses at a red-heat, and at a higher temperature sublimes in white vapor: it is soluble in alcohol and in ether, in acetic and hydrochloric acids, and in ammonia. It consists of

						Berthmot.
Zinc.....	1	...	32	...	29.2	29.25
Bromine	1	...	78	...	70.8	70.75
<hr/>						
Bromide of zinc	1		110		100.0	100.00

BROMATE OF ZINC. ZnO,BrO_5 . By dissolving hydrated oxide of zinc in aqueous bromic acid, and evaporating, cubo-octohedral crystals =

$\text{ZnO}, \text{BrO}_5, 6\text{HO}$, are obtained, soluble in their weight of cold water: they become anhydrous when dried at 390° . (RAMMELSBERG. *Poggend.*, lii. 90.)

FLUORIDE OF ZINC is very difficultly soluble: with fluoride of potassium it forms a more soluble triple salt. (BERZELIUS.)

NITRATE OF ZINC. $\text{ZnO}, \text{NO}_5, 6\text{HO}$, is a deliquescent salt, which crystallizes with difficulty in four-sided prisms terminated by four-sided pyramids. They are copiously soluble in water and in alcohol; when thrown upon glowing coals they are decomposed, and give to flame a bluish-green color. The action of strong nitric acid upon zinc is so intense, as sometimes it is said to produce ignition; during the decomposition, nitrous and nitric oxide, and ultimately nitrogen, are evolved, and some ammonia is formed. The crystals of nitrate of zinc contain about 36 *per cent.* of water, equivalent to 6 atoms, 3 atoms of which escape at 212° , but the remaining 3 atoms cannot be expelled without the decomposition of the salt: they consist of

						Graham.	
Oxide of zinc	1	...	40	...	27.0	...	26.94
Nitric acid	1	...	54	...	36.5	...	
Water	6	...	54	...	36.5	...	
<hr/>						<hr/>	
Crystallized nitrate of zinc	1		148		100.0		

Two *subnitrates of zinc* have been described by Grouvelle and Schindler: one, formed by heating the nitrate, or precipitating it by a small addition of ammonia $= 8\text{ZnO}, \text{NO}_5, 2\text{HO}$: the other by digesting this in a solution of the nitrate $= 4\text{ZnO}, \text{NO}_5, 2\text{HO}$.

AMMONIA AND OXIDE OF ZINC. Hydrated oxide of zinc dissolves in aqueous ammonia, forming a colorless liquid, which, if saturated, becomes turbid on dilution: the crystals which it occasionally deposits are those of hydrated oxide or carbonate of zinc. Metallic zinc immersed in ammonia in contact with iron evolves hydrogen, and is slowly dissolved. Oxide of zinc which has been ignited is only very difficultly and sparingly dissolved by ammonia, but the presence of traces of several of the salts of ammonia and of potassa remarkably facilitates the solution, especially of the phosphates.

SULPHURET OF ZINC. ZnS , exists native under the name of *Blende*. It may be formed artificially by heating oxide of zinc with excess of sulphur, and is then of a yellow brown color. It is also produced by heating rapidly and suddenly a mixture of zinc filings and sulphuret of mercury: the mercury is revived, and intense action ensues during the union of the zinc and sulphur. By passing the vapor of sulphur over fused zinc, E. Davy obtained a white crystalline substance resembling native phosphorescent blende. When a salt of zinc is precipitated by hydrosulphuret of potassa, a white compound is obtained, composed, according to Berzelius, of 72 oxide of zinc, 25 sulphuretted hydrogen, 3 water. It is probably a monohydrated sulphuret of zinc. Berthier formed a yellow crystalline sulphuret of zinc by heating anhydrous sulphate of zinc white-hot for an hour in a crucible lined with charcoal. It is observed by Dumas, that, considering the strong affinity of zinc for oxygen and chlorine, its feeble affinity for sulphur is remarkable. Hydrogen and charcoal decompose

blende at a white heat; in the former case sulphuretted hydrogen, and in the latter, sulphuret of carbon is formed.

Hydrated sulphuret of zinc is the result of the decomposition of zinc salts by sulphuretted hydrogen or alkaline hydrosulphurets; it is white, and when dried at 100° , or in vacuo, is $\text{ZnS}\cdot\text{HO}$: dried at 212° , it loses half its water, which it regains by exposure to air. (GMELIN.)

Sulphuret of zinc, native or artificial, consists of

						Arfwedson.	Thomson.		
Zinc.....	1	...	32	...	66.7	...	66.34	...	67.19
Sulphur	1	...	16	...	33.3	...	33.66	...	32.81
<hr/>									
Sulphuret of zinc....	1		48		100.0		100.00		100.00

Native Sulphuret of Zinc, or *Blende*, occurs in crystals which are brittle, soft, and of different shades of brown and black. Its primitive form is the rhomboidal dodecahedron. It usually contains traces of iron and lead. It is an abundant mineral, and important as a source of the pure metal, which is obtained by roasting the ore, and afterwards exposing it to heat in proper distillatory vessels, mixed with charcoal. The English miners call it *black jack*.

OXYSULPHURET OF ZINC. When hydrogen is passed over sulphate of zinc at a high temperature, a pulverulent residue is obtained, composed of 1 atom of oxide and 1 of sulphuret of zinc. Karsten analyzed some hexagonal crystals which lined one of the zinc-furnaces at Freiburg, and found them composed of 4 atoms of sulphuret and 1 atom of oxide of zinc. (DUMAS.)

HYPOSULPHITE OF ZINC. $\text{ZnO}\cdot\text{S}_2\text{O}_2$, was obtained long ago by Fourcroy, who considered it as a *sulphuretted sulphite*: he formed it by digesting metallic zinc in sulphurous acid. By gentle evaporation crystals are obtained, which are to be digested in alcohol; this liquid dissolves the hyposulphite, and affords it in prismatic crystals; the sulphite which is at the same time formed being insoluble in alcohol. A mixture of oxide of zinc and sulphur treated by sulphurous acid, affords the same salt; it is efflorescent, and easily decomposed by heat. (FOURCROY, *Système des Connoissances Chimiques*, v. 380.)

This salt has been more lately examined by Fordos and Gélis; they state that its solution is colorless and inodorous, and not precipitated by alcohol: they could not obtain it solid or crystallized, for if evaporated, either spontaneously or in vacuo, when it has attained a certain degree of concentration, the solution becomes turbid from the deposition of a white sulphuret of zinc, and sulphuretted hyposulphate of zinc is formed. This decomposition, common to other hyposulphites, is represented by this equation: $2[\text{ZnO}\cdot\text{S}_2\text{O}_2] = \text{ZnS} + [\text{ZnO}\cdot\text{S}_3\text{O}_5]$. When the solution of hyposulphite of zinc is evaporated to dryness, the final result is sulphuret of zinc, sulphur, sulphate of zinc, and a disengagement of sulphurous acid.

HYPOSULPHITE OF ZINC AND AMMONIA. $\text{NH}_3\cdot\text{ZnO}\cdot\text{S}_2\text{O}_2$. Acicular crystals obtained by supersaturating a solution of hyposulphite of zinc with ammonia, and adding alcohol: it is decomposed by water, with the deposition of oxide. (RAMMELSBERG. *Poggend.*, lvi. 62.)

SULPHITE OF ZINC. ZnO, SO_2 , is formed by dissolving the oxide in sulphurous acid; it is more easily crystallizable and much less soluble in water than the hyposulphite, and is insoluble in alcohol. Its formula, according to Fordos and Gélis, (*Ann. Ch. et Ph.*, Juillet, 1843) is $\text{ZnO}, \text{SO}_2, 2\text{HO}$.

HYPOSULPHATE OF ZINC. $\text{ZnO}, \text{S}_2\text{O}_5$, is obtained by adding a solution of hyposulphate of baryta to sulphate of zinc; it is very soluble, difficultly crystallizable, and decomposed by a slight elevation of temperature: by boiling it becomes sulphate. The crystals are composed of

	Heeren.					
Oxide of zinc	1	40	24.1 24.25
Hypsulphuric acid.....	1	72	43.4 43.51
Water	6	54	32.5 32.24
<hr/>						
Crystals of hyposulphate of zinc.....	1		166		100.0	100.00

HYPOSULPHATE OF ZINC AND AMMONIA. $\text{ZnO}, \text{NH}_3, \text{S}_2\text{O}_5$, is precipitated in small prismatic crystals, on the cooling of a hot concentrated solution of hyposulphate of zinc in ammonia: it is decomposed by water. (RAMMELSBERG.)

SULPHATE OF ZINC. ZnO, SO_3 . Zinc is readily oxidized and dissolved by dilute sulphuric acid, and hydrogen gas is given off; the zinc so decomposes water, that an atom of zinc is substituted for an atom of hydrogen: $\text{HO}, \text{SO}_3 + \text{Zn} = \text{ZnO}, \text{SO}_3 + \text{H}$: or, consistently with the results of electrolysis as pointed out by Daniell, $\text{H}, \text{SO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{H}$. A transparent colorless solution of *sulphate of zinc* results, which by evaporation affords crystals $= \text{ZnO}, \text{SO}_3, 7\text{HO}$, sp. gr. 2.036, in the form of right rhombic prisms. (BROOKE, *Ann. of Phil.*, N.S., vi. 437.) This salt is usually stated to be soluble in 2.5 parts of water at 60° ; but according to Karsten 1 part of the crystals are soluble in 0.923 of water at 60° , forming a solution of the sp. gr. 1.4235: they are even more soluble in hot water: alcohol takes up a mere trace. The crystals are slightly efflorescent: at 212° they lose 6 atoms of water, retaining 1 till heated nearly to dull redness. The *anhydrous sulphate* is white and friable: sp. gr. 3.4: exposed to humid air it gradually resumes 7 atoms of water: it heats when sprinkled with water: at a high temperature it evolves sulphuric and sulphurous acids and oxygen, and at a white-heat is entirely decomposed, leaving oxide of zinc. Hydrogen passed over the red-hot salt converts it into *oxisulphuret*. It is soluble in hydrochloric acid without decomposition. Anhydrous sulphate of zinc consists of

	Tennant.						Wenzel.	Thomson.
Oxide of zinc.....	1	40	50	46.19 52.23
Sulphuric acid	1	40	50	53.81 47.77
<hr/>								
Sulphate of zinc.....	1		80		100		100.00	100.00

The ordinary crystals are constituted of

	Mitscherlich.						Kühn.		
Anhydrous sulphate of zinc....	1	...	80	...	56	...	55.24	...	55.72
Water	7	...	63	...	44	...	44.76	...	44.28
<hr/>									
Crystals of sulphate of zinc	1		143		100		100.00		100.00

The crystals formed at a temperature exceeding 86° contain 6 equivalents of water, and are in the form of an oblique rhombic prism. (MITSCHERLICH.) When sulphuric acid is added to a concentrated solution of sulphate of zinc, a white pulverulent sulphate falls, containing 2 equivalents of water. So also when the pulverised crystals of the common sulphate are digested in absolute alcohol they leave a binhydrated salt. Boiled in alcohol of sp. gr. 0.856 a crystalline mass of pentahydrated sulphate remains. (KÜHN.)

White vitriol, or the sulphate of zinc of commerce, is often obtained by the oxidizement of blende, and is therefore very impure; it generally contains a subsulphate of zinc, together with the sulphates of iron, copper, cadmium, alumina, and sometimes lead. It usually occurs in amorphous masses with a fracture a little resembling that of sugar.

Native Sulphate of Zinc occurs at Holywell in Flintshire, and in other places where the sulphuret of zinc is found; it is probably the result of the decomposition of that ore, and is often contained in the waters of the mines.

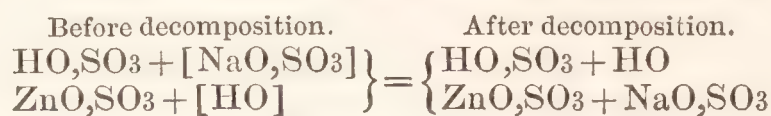
Subsulphates of Zinc. 1. *Bibasic.* $2\text{ZnO},\text{SO}_3$, is formed by digesting metallic zinc or oxide of zinc in a concentrated solution of the neutral sulphate: or by throwing down the oxide from one-half of a solution of the neutral sulphate, and adding it to the other half; it does not crystallize, but by slow evaporation or when copiously diluted, deposits *octobasic* sulphate $= 8\text{ZnO},\text{SO}_3,2\text{H}_2\text{O}$. (SCHINDLER.) 2. *Quadribasic.* $4\text{ZnO},\text{SO}_3$, is obtained by precipitating the sulphate by a quantity of potassa insufficient for its entire decomposition, and dissolving the precipitate in boiling water: it crystallizes either in plates or prisms, and may be obtained with 2, 4, 8, and 10 atoms of water. (KÜHN. GMELIN, *Handbuch*.)

SULPHATE OF ZINC AND AMMONIA. 100 parts of anhydrous sulphate of zinc rapidly absorb 53.7 of ammonia, with the production of heat: the compound dissolved in water deposits oxide of zinc. (H. ROSE, *Ann. Ch. et Ph.*, lii. 311.) Thomson obtained an ammonio-sulphate $= \text{NH}_4\text{O},\text{ZnO},2\text{SO}_3,6\text{H}_2\text{O}$, by mixing solutions of the two constituent salts in atomic proportions, and concentrating by evaporation: it crystallizes in white rhomboids, which readily dissolve in water. By the action of excess of ammonia on a solution of sulphate of zinc a salt is formed, the formula of which is $\text{NH}_4\text{O},\text{SO}_3 + \text{NH}_3,\text{ZnO}$: it crystallizes in short prisms, and when heated evolves $\text{NH}_3,\text{H}_2\text{O}$, and a white powder, $\text{NH}_3,\text{ZnO},\text{SO}_3$, remains: in crystals it contains $3\text{H}_2\text{O}$, of which it loses 2 by efflorescence, and the third by a moderate heat. (KANE, *Elements*.)

SULPHATE OF ZINC AND POTASSA. $\text{KO},\text{ZnO},2\text{SO}_3,6\text{H}_2\text{O}$, forms flat rhomboidal crystals, permanent in the air, and soluble in 5 parts of water at 60° . (II. STOKES, *Phil. Mag.*, 2nd Series, ii. 428.) They lose 5 atoms of water in vacuo, at 80° : the remaining atom of water is retained till heated to 250° . (GRAHAM.)

SULPHATE OF ZINC AND SODA. $\text{NaO},\text{ZnO},2\text{SO}_3,4\text{H}_2\text{O}$. Sulphate of zinc and sulphate of soda when simply dissolved together always crystallize apart and do not combine: but the double salt is formed on mixing

strong solutions of sulphate of zinc and bisulphate of soda, and separates by crystallization, the sulphate of water with constitutional water (hydrated acid of sp. gr. 1.78) being produced at the same time and remaining in solution. The reaction which occurs may be thus expressed:



in which the constituents of both salts inclosed in brackets, are found to have exchanged places after decomposition, without any other change in the original salts. (GRAHAM. *On water as a constituent of the sulphates. Phil. Mag.*, 3rd Series, vi. 417.) According to Karsten, (as quoted by Gmelin,) this double salt may be obtained by dissolving sulphate of zinc in a saturated solution of sulphate of soda, and leaving it slowly to evaporate: and it is only when the solution is strongly heated and then suddenly cooled, that the salts separate.

SULPHATE OF ZINC AND MAGNESIA. Sulphate of magnesia dissolved in a cold saturated solution of sulphate of zinc, is at first clear, but afterwards deposits a double salt. (KARSTEN.) According to Pierre, this salt is $\text{ZnO,SO}_3 + \text{MgO,SO}_3 + 14\text{HO}$. He considers the sulphate of zinc as carrying its 7 atoms of water into its double salts. (*Ann. Ch. et Ph.*, Feb. 1846.)

PHOSPHURET OF ZINC is a brilliant lead-colored compound, formed by distilling in a coated retort a mixture of 2 parts of zinc and 1 of phosphorus: it rises as a sublimate. When phosphuretted hydrogen is gently passed over warm chloride of zinc, hydrochloric acid is slowly evolved, and on dissolving the mass in water, black particles of a metallic lustre separate, insoluble in hydrochloric acid, and burning before the blow-pipe with a phosphorus flame. (H. ROSE.)

HYPOPHOSPHITE OF ZINC. The solution of oxide of zinc in warm aqueous hypophosphorous acid evaporated in vacuo leaves a crystalline residue of this salt. (H. ROSE.) It forms octohedrons and rhombohedrons which are extremely efflorescent: their formula is ZnO,PO,3HO . (WURTZ.)

PHOSPHITE OF ZINC. $\text{ZnO,PO}_3,6\text{HO}$. This is a difficultly-soluble salt, obtained by adding an aqueous solution of terchloride of phosphorus saturated with ammonia to a solution of sulphate of zinc: it is partly precipitated and the rest may be obtained by evaporation. (H. ROSE, *Poggend.*, ix. 29.)

PHOSPHATE OF ZINC. (1.) *Tribasic.* 3ZnO,PO_5 . When phosphate of soda is added to solution of sulphate of zinc a precipitate falls, at first gelatinous, but afterwards granular, tasteless, and easily fusible: insoluble in water, but easily soluble in acids, and in ammonia.

(2.) *Tribasic, with 1 atom of water.* 2ZnO,HO,PO_5 . This salt falls in small shining crystals on mixing a solution of 3 parts of sulphate of zinc in 32 of hot water, with one of 4 parts of crystallized phosphate of soda in 32 of hot water: the crystals are $2\text{ZnO,HO,PO}_5 + 2\text{HO}$. At a heat above 212° , but below that of melting tin, they lose 2 atoms

of water: they fuse at a red heat, losing the third atom of water. (GRAHAM.)

Pyrophosphate of Zinc is formed by precipitating a zinc-salt with pyrophosphate of soda: boiled in solution of common phosphate of soda, it yields common phosphate of zinc and pyrophosphate of soda. (STROMAYER.)

CARBURET OF ZINC is the black powder which remains after the distillation of cyanide of zinc. (BERZELIUS.)

CARBONATE OF ZINC. ZnO, CO_2 , may be formed by passing carbonic acid through water containing diffused hydrated oxide of zinc. The precipitate formed by adding carbonate of potassa to sulphate of zinc, is, according to Berzelius, a mixture of carbonate and hydrated oxide, analogous to the *magnesia alba*: its formula being $2[\text{ZnO}, \text{CO}_2] + 3[\text{ZnO}, \text{HO}]$, or when precipitated in the cold, $\text{ZnO}, \text{CO}_2 + 2[\text{ZnO}, \text{HO}]$. Some of the varieties of *calamine* consist of anhydrous carbonate of zinc: specimens from Somersetshire and Derbyshire yielded

						Smithson.		
Oxide of zinc	1	...	40	...	64.5	...	65
Carbonic acid	1	...	22	...	35.5	...	35
		<hr/>		<hr/>		<hr/>		<hr/>
		1		62		100.0		100

Another variety of *calamine*, from Bleiberg, in Carinthia, is probably a hydrous subcarbonate, consisting of

					Smithson.		
Oxide of zinc	3	...	120	...	71	...	71.4
Carbonic acid	1	...	22	...	13	...	13.5
Water.....	3	...	27	...	16	...	15.1
	<hr/>		<hr/>		<hr/>		<hr/>
	1		169		100		100.0

Calamine occurs both crystallized and massive; its primitive form is an obtuse rhomboid. It is often found investing carbonate of lime, which has sometimes been decomposed, and the *calamine* remains in pseudocrystals. It abounds in Somersetshire, Flintshire, and Derbyshire. A beautiful variety, colored by carbonate of copper, is found at Matlock. The variety of *calamine*, known by the name of *electric calamine*, from its property of becoming electrical when gently heated, consists of oxide of zinc in combination with silica.

AMMONIO-CARBONATE OF ZINC is formed by precipitating carbonate of zinc, and, having washed it upon a filter, pouring upon it a concentrated solution of carbonate of ammonia; the filtrate gradually deposits acicular groups of the double salt $= 2\text{ZnO}, \text{NH}_4 \text{O} + 2\text{CO}_2$. (FAVRE, *Ann. Ch. et Ph.*, Avril, 1844.) Zinc filings and oxide of zinc both dissolve in aqueous carbonate of ammonia, the former effervescing, the latter heating. The evaporated liquor yields silky crystals which are decomposed by excess of water. When solution of chloride of zinc is dropped into excess of ammonia and carbonate of ammonia added, stellated groups of acicular crystals form upon exposing the solution to air: when dried, they become white and crumble into a powder, which leaves when heated 62 per cent. of oxide of zinc. (WÖHLER.)

POTASSIO-CARBONATE OF ZINC is deposited as a white powder, $\text{KO}, \text{ZnO}, 2\text{CO}_2, 2\text{HO}$, when a saturated solution of oxide of zinc in potassa is exposed to the air. (KANE.)

SODIO-CARBONATE OF ZINC. When zinc is boiled for some hours in a solution of carbonate of soda, hydrogen is evolved, and oxide of zinc dissolved: after some days the undissolved zinc is covered with small octohedral and tetrahedral crystals insoluble in water, but from which, after they have been heated red-hot, water abstracts carbonate of soda and leaves oxide of zinc. (WÖHLER.)

CYANIDE OF ZINC, ZnCy , forms an insoluble white powder, when solution of cyanide of potassium is added to sulphate of zinc; or when hydrocyanic acid is added to acetate of zinc; it is insoluble in alcohol, but soluble in ammonia, and in dilute hydrochloric acid, with the separation of hydrocyanic acid. By destructive distillation in a retort, it leaves a black *carburet of zinc*.

FULMINATE OF ZINC. $2\text{ZnO}, \text{Cy}_2 \text{O}_2$. When 1 part of fulminating mercury and 2 of zinc filings are shaken together with a little water in a phial an amalgam of zinc is formed, and the solution holds fulminate of zinc without a trace of mercury: evaporated in vacuo it deposits small white rhomboidal crystals and a yellow powder which may be washed off with water: the crystals are insoluble in water; they explode at 350° , and also by friction, and by contact of sulphuric acid. When baryta is added to the original solution of this salt half the oxide of zinc is thrown down and *zincofulminate of baryta* is obtained $= \text{ZnO}, \text{BaO}, \text{Cy}_2 \text{O}_2$. From this the baryta may be precipitated by sulphuric acid, and an acid fulminate of zinc is retained in solution. Decomposed by sulphate of potassa, the baryta salt gives rise to a *zincofulminate of potassa*, $\text{ZnO}, \text{KO}, \text{Cy}_2 \text{O}_2$. In the same way other zincofulminates may be obtained. (E. DAVY.) Other views of the constitution of these salts have been taken by Berzelius. (*Handbuch.*)

FERROCYANIDE OF ZINC is thrown down in the form of a white gelatinous precipitate, when hydroferrocyanic acid is added to a soluble zinc-salt.

ZINCOCYANIDE OF POTASSIUM. When cyanide of zinc is dissolved in a solution of cyanide of potassium, filtered, and evaporated, large octohedral crystals are obtained, anhydrous, decrepitating when heated, and then fusing into a transparent colorless liquid. (L. GMELIN.)

FERROCYANIDE OF ZINC AND POTASSIUM. When a solution of ferrocyanide of potassium is added to a zinc-salt, the white precipitate which falls is a double ferrocyanide. It is represented by the formula $\text{Zn}_3, \text{K}: 2\text{Cfy}$. When dried in the air it retains 12 atoms of water. (MOSANDER.)

REDUCTION OF THE ORES OF ZINC. The zinc of commerce is procured from the native sulphuret, and from calamine, by the following process. The ore is first picked and broken into small pieces, and then

submitted to a dull red-heat in a reverberatory furnace, by which carbonic acid is driven off from the calamine, and sulphur from the blende. It is then washed, ground, and thoroughly mixed with about one-eighth its weight of powdered charcoal. This mixture is put into large earthen pots, not unlike oil-jars, six of which are usually placed in a circular furnace; each pot has an iron tube passing from its lower part, through the floor of the furnace, and dipping into water; they are everywhere else firmly luted: upon the application of a high red heat, the metal distils through the tube into the water beneath, whence it is collected, melted, and cast into cakes. The details of the process for the reduction of zinc will be found in URE's *Dict. of Arts and Manufactures*, and in DUMAS, *Chim. app. aux Arts*.

ALLOYS OF ZINC. With *potassium* and *sodium*, zinc forms brittle alloys, decomposable by exposure to air and water. Its alloy with *manganese* is unknown. With *iron* it yields a white and somewhat malleable alloy, which is difficult to form; but if plates of hot iron be dipped into melted zinc, they acquire the appearance of tin-plate, for which they are a most valuable substitute, inasmuch as the zinced iron is prevented from oxidizement and rusting by the electrical relations of the metals (p. 225): the zinc it is true is more subject to oxidizement, but so long as any of it remains the iron is protected; and, when covered by a coat of paint, is extremely durable. Hurdles, fences, and all out of door iron-work, as well as locks, bolts, hinges, and other implements used in damp situations, and all iron-work employed in the contact of water, may be thus defended. Zinced iron has also been of late used for roofing, and is extensively thus applied in the new palace at Westminster; it has also been successfully employed as a substitute for the copper-sheathing of ships. The wires of electric telegraphs are generally of zinced iron, and their section, when exposed to air and water, sometimes exhibits a fresh deposition of zinc, arising from the galvanic precipitation of small portions of dissolved zinc upon the electro-negative iron: in short, zinced iron promises to rank amongst the most important contributions of science to the useful arts. The zinging of iron is generally performed by dipping the iron, previously well cleaned, into melted zinc the surface of which is kept carefully covered with sal-ammoniac to prevent oxidizement, and so enable the iron to become thoroughly wetted as it were, and superficially combined with the zinc. The zinc is fused in large wrought iron vessels, placed over proper furnaces. and after the frequent dippings of the iron articles, there is ultimately found at the bottom of the melted metal a quantity of a granular alloy of zinc and iron. The process is not applicable to the generality of vessels used for culinary purposes, in consequence of the contaminations by oxide of zinc which would often ensue, especially with acidulous liquors. In using zinced iron care should be taken that where nails or rivets are required they should also be of the same material.

CHARACTERS OF THE SALTS OF ZINC. They are mostly soluble in water, and the solutions are colorless, and have a peculiarly unpleasant astringent and metallic taste: they are not precipitated by iodide of potassium. Potassa, soda, and ammonia, form white precipitates, soluble

in excess of the alkali, and in dilute sulphuric acid. In this case the precipitate is distinguished from alumina by its solubility in excess of ammonia. The precipitate formed in solutions of zinc by the carbonates of potassa and soda is not soluble in excess of those carbonates, but when carbonate of ammonia is used the precipitate is again dissolved. Sulphuretted hydrogen throws down a white hydrated sulphuret of zinc in some of the perfectly neutral solutions, but not in those which are acid or alkaline. Hydrosulphuret of ammonia produces a white or yellowish-white precipitate. The soluble phosphates, carbonates, oxalates, and borates, produce white precipitates soluble in acids and alkalis: ferrocyanide of potassium gives a white bulky precipitate, and ferridcyanide an orange-colored precipitate, soluble in hydrochloric acid. Infusion of galls occasions no precipitate except in the basic salts. The salts which are insoluble in water dissolve in dilute sulphuric acid, and are precipitated by ammonia, but generally dissolve in excess of acid or of precipitant. Metallic zinc is not thrown down from its solutions by any of the other metals, with the occasional exception, however, of iron. (See p. 195.)

Before the blow-pipe *oxide of zinc* becomes yellow when heated, but whitens as it cools. A small proportion forms with microcosmic salt, and with borax, a clear glass, which becomes opaque on increasing the quantity of oxide. A drop of nitrate of cobalt being added to the oxide, and dried and ignited, it becomes green. With soda, in the interior flame oxide of zinc is reduced, and the metal burns with its characteristic flame, depositing its oxide upon the charcoal. By this process zinc may be easily detected, even in the *automalite*. Mixed with oxide of copper, and reduced, the zinc will be fixed and brass obtained. But one of the most unequivocal characters of the oxide of zinc is, to dissolve it in acetic acid, evaporate the solution to dryness, and expose it to the flame of a lamp, when the metal is reduced and burns with its peculiar flame.

§ XI. TIN. Sn. 59.

TIN (Jupiter ♃ of the alchemists) has been known from the remotest ages. It was in common use in the time of Moses, and was obtained at a very early period from Spain and Britain by the Phœnicians. (PLINY, lib. iv. cap. 34, and xxxiv. cap. 47.) It occurs most abundantly in Cornwall; and is also found in Germany, Bohemia, and Hungary, in Europe; in Chili and Mexico; in the Peninsula of Malacca; and in India, in the Island of Banca. A little tin has also been found at Fahlun and Utö, in Sweden. Several varieties of tin occur in commerce, respecting which Vauquelin has given an useful essay. (*Ann. de Chim.*, LXXVII.) The *native peroxide* is the principal *ore of tin*: the metal is obtained by heating it to redness with charcoal or culm, and a little lime; the first product is impure and is returned into the furnace, and carefully heated so as to fuse the tin, which runs off into an iron kettle, while the principal impurities remain unmelted; in the kettle the tin is kept in fusion, stirred, and agitated by plunging wet charcoal into it, by which a quantity of impurities collect upon the surface, and are removed by a skimmer; thus refined, the metal is cast into blocks of about 3 cwt. each. The common ores are known under the name of *mine tin*, and furnish a

less pure metal than that obtained from *stream tin*. The ordinary processes of reduction are described at length in AIKIN'S *Dictionary* (Art. TIN); by M. Bonnard (*Journ. des Mines*, xiv.); and by Mr. Taylor, in the 5th volume of the *Geological Transactions*. The purest kind of tin is known in commerce under the name of *grain tin*, a term formerly applied exclusively to the metal obtained from the stream ore: *block tin* is less pure, and is the produce of the common ore of the veins. The peculiar columnar fracture which pure or grain tin exhibits when broken, is given it by heating the mass till it becomes brittle, and then letting it fall upon a hard pavement from a height.

Tin has a silvery-white color with a slight tint of yellow, and when so viewed as to exclude the white light reflected from its surface, it is decidedly yellow; it is softer than gold, but harder than lead; it is malleable, though sparingly ductile. Common tin-foil, which is obtained by beating out the metal, is often not more than 1-1000th of an inch in thickness, and what is termed *white Dutch metal* is in much thinner leaves.

Its specific gravity fluctuates from 7.28 to 7.6, the lightest being the purest metal. Its specific heat is 0.05623. (REGNAULT.) When bent, it occasions a peculiar crackling noise, arising from the destruction of cohesion among its particles, and hence the brittleness and want of tenacity of tin-wire. When a bar of tin is rapidly bent backwards and forwards several times successively, it becomes so hot that it cannot be held in the hand. When rubbed it exhales a peculiar odor. It melts at 442° (CRICHTON. RUDBERG.) 446° (KUPFFER), and slightly contracts on consolidation. By exposure to heat and air, it is gradually converted into protoxide; but if the heat be continued till metallic tin no longer remains, the protoxide passes into peroxide. Placed upon ignited charcoal under a current of oxygen gas, it enters into rapid combustion, forming the peroxide; and if an intensely-heated globule of the metal be thrown upon a sheet of dark-colored paper, it subdivides into small particles, which burn very brilliantly, and leave lines of white oxide. It volatilizes at a very high temperature. When a polished surface of tin is heated it becomes yellow and iridescent, in consequence of superficial oxidizement.

A preparation, under the name of *powdered tin*, is sometimes directed to be made for pharmaceutical use, by shaking the melted metal in a wooden box rubbed with chalk on the inside: *tin filings* have also a place in some *Pharmacopœiæ*, and have been used as a vermifuge. These preparations are, however, both dangerous, the metal being rendered poisonous in the former case by slight oxidation, (ORFILA, *Traité des Poisons*, tom. i. 2me partie, p. 18,) and often creating dangerous irritation when given in filings. The equivalent of tin may be assumed as 59. (57.9 TURNER; 59 GMELIN; 58.92 GRAHAM.)

PROTOXIDE OF TIN. STANNOUS OXIDE, SnO, is obtained by precipitating a solution of protochloride of tin by ammonia; it falls in the state of *hydrate*; when dried, out of the contact of air, it is of a dark color, and undecomposable alone by heat. According to Cassola, protoxide of tin is formed by pouring nitric acid diluted with ten times its volume of water

upon tin filings, and leaving them in contact 48 hours. When protochloride of tin is decomposed by a carbonated alkali, and the precipitate carefully dried at a temperature below 212° , it is also a *hydrated protoxide*, retaining no trace of carbonic acid. It is obtained *anhydrous* by heating the hydrate to redness in a retort filled with carbonic acid; or by heating it in a glass tube, and passing a current of dry carbonic acid over it till the water is carried off, and suffering it to cool out of the contact of air. The best process for obtaining the anhydrous protoxide appears to be the decomposition of fused protochloride of tin by carbonate of soda: 1 atom of each are fused together and stirred till the mixture acquires a black color: it is then washed, and the remaining protoxide dried at a gentle heat. (SANDALL.) The specific gravity of this oxide is 6.6. It is in the form of a dark grey or black powder, which, on the contact of a red-hot wire, burns like tinder into peroxide. In the hydrated state it dissolves very readily in sulphuric, hydrochloric, and dilute nitric acids, and in caustic potassa and soda, but not in ammonia, nor in the alkaline carbonates. Its alkaline solution, when long kept, deposits metallic tin in arborescent crystals, and becomes a solution of the peroxide. The presence of protoxide of tin in solution is announced by its action on chloride of gold, with which it forms a purple precipitate. Protoxide of tin consists of

						Berzelius.		Proust.		Gay Lussac.	
Tin.....	1	...	59	...	88.06	...	88.028	...	87	...	88.1
Oxygen	1	...	8	...	11.94	...	11.972	...	13	...	11.9
<hr/>											
Protoxide of tin....	1		67		100.00		100.000		100		100.0

SESQUIOXIDE OF TIN. DEUTOXIDE OF TIN. Sn_2O_3 . When a solution of protochloride of tin is mixed with moist hydrated sesquioxide of iron and boiled, an interchange of elements takes place, by which protochloride of iron and sesquioxide of tin are formed: in this case, $2[\text{SnCl}]$ and Fe_2O_3 , become Sn_2O_3 and $2[\text{FeCl}]$. The solubility of this oxide in ammonia distinguishes it from protoxide; and its giving a purple precipitate with chloride of gold, from peroxide: it is soluble in concentrated hydrochloric acid. (FUCHS.)

PEROXIDE OF TIN. BINOXIDE OF TIN. STANNIC OXIDE. STANNIC ACID. SnO_2 , is the result of the combustion of tin at high temperatures, (*Flores Jovis*.) It is also formed by passing steam over red-hot tin, (GAY LUSSAC,) and by heating a mixture of 1 part of tin filings with 4 of peroxide of mercury, in a retort. (BERZELIUS.) It is generally prepared by treating the metal with nitric acid: in its most concentrated form this acid does not immediately act, but on the addition of a few drops of water violent effervescence ensues, much heat is evolved, together with nitric oxide and nitrous acid vapor some nitrate of ammonia is also formed, and the peroxide of tin remains in the form of a white insoluble powder; it may be purified by washing it with boiling distilled water, and may then be dried at a dull red-heat. Peroxide of tin is also formed by projecting a sufficient quantity of nitre upon red-hot tin. Fused with glass, it forms *white enamel*; but alone, it is extremely infusible, and when it has been heated it is insoluble in acids. The substance called *Tin putty*, or

Jewellers' putty, is an oxide of tin, formed by levigating the crusts of oxide that form upon the metal when kept for some time in fusion: it is probably a mixture of the protoxide and peroxide, and is used for polishing hard bodies.

When a solution of bichloride of tin is decomposed by ammonia, or by an alkaline carbonate, a bulky gelatinous precipitate falls, which, when washed and carefully dried, resembles gum: it is a *hydrated peroxide*, and retains one atom of water. In this state it is soluble in the acids: dilute hydrochloric acid dissolves it abundantly; but if it be boiled in water, and then again collected and dried, it is no longer perfectly soluble in hydrochloric acid, but forms with it a subsalt; on pouring off the excess of acid the residue may be dissolved in water, but when hydrochloric acid is added it is again thrown down. These peculiarities have been referred to changes in its state of hydration. If the hydrated peroxide obtained by the action of nitric acid on tin be heated to redness, it becomes insoluble in the acids unless previously ignited with potassa or soda. This oxide consists of

				John Davy.	Proust.	Gay Lussac.	Berzelius.
Tin.....	1	59	78·67	78·34	78·4	78·6	78·62
Oxygen	2	16	21·33	21·66	21·6	21·4	21·38
Peroxide of tin	1	75	100·00	100·00	100·0	100·0	100·00

Berzelius has shown (*Lehrbuch*) that the oxide of tin obtained by the decomposition of the perchloride, has characters distinct from those of the peroxide obtained by the action of nitric acid on tin: the former he terms modification *a* or $a\text{SnO}_2$; the latter, modification *b* or $b\text{SnO}_2$. The former ($a\text{SnO}_2$) is soluble in its hydrated state in nitric acid, which gradually deposits it in gelatinous lumps, coagulated when heated to 122° , and in this state, if treated first by ammonia and then by nitric acid, it is soluble. It is soluble in dilute sulphuric acid, and the solution is not precipitated when boiled. It is easily dissolved by hydrochloric acid, and excess of acid does not precipitate it. The latter ($b\text{SnO}_2$) is insoluble in nitric acid, and in sulphuric acid, and nearly insoluble in hydrochloric acid, with which, however, it combines, so that when the acid is poured off, the residue, after having been washed with a little water, is soluble in water, but again precipitated from its aqueous solution by hydrochloric acid.

Native Peroxide of Tin is generally grey, brown, or black, and sometimes transparent or translucent. The specific gravity of the native oxide is 7: its primitive crystal is an obtuse octohedron, of which the modifications are extremely numerous. (W. PHILLIPS, *Geol. Trans.*, ii.) In some of the valleys of Cornwall, tin is found in rounded nodules, of various sizes, mixed with pebbles and rounded fragments of rocks. To separate the tin from the alluvial matter, currents of water are passed over it, and hence these deposits have been called *stream works*, and the tin ore, *stream tin*. One of the most extensive of these is a branch of Falmouth Harbour. A modification of stream tin is called *wood tin*: it usually appears in small banded fragments of globular masses. The native peroxide of tin is insoluble in the acids, but if it be fused with potassa, the resulting stannate of potassa is soluble in water, and from it the soluble hydrated peroxide may be thrown down by the acids.

The following are analyses of native oxide of tin from several localities (DUMAS):

	Cornwall.		Bohemia.		Mexico.		Finbo.		Wood tin.
Peroxide of tin.....	99·00	99·5	95·0	93·6	91
Oxide of iron	0·25	0·5	5·0	1·4	9
Oxide of manganese....	0·00	0·0	0·0	0·8	0
Silica.....	0·75	0·0	0·0	0·0	0
Oxide of columbium	0·00	0·0	0·0	2·4	0
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	100·00		100·0		100·0		98·2		100

PROTOCHLORIDE OF TIN. SnCl . Anhydrous protochloride of tin is obtained by subjecting a mixture of equal weights of calomel and of an amalgam of tin and mercury to distillation, in a retort gradually raised to a dull-red heat; or a mixture of 1 part of tin filings and 2 of corrosive sublimate may be treated in the same way. When hydrochloric acid gas is passed over heated tin in a glass tube, the protochloride is also formed, and hydrogen gas is given off. When tin is dissolved in hydrochloric acid, the solution evaporated, and the dry residue carefully heated to incipient redness in a small tube retort so as to exclude the action of air, the protochloride of tin remains nearly pure. It is in the form of a grey solid, of a resinous lustre, fusible and volatile at a high heat. (*Butter of Tin*.) When its solution in a small quantity of water is evaporated, it yields either acicular or prismatic crystals, which include 3 atoms of water, and of which the greater part may be expelled at 212° . When a large quantity of water is poured upon these crystals they are partly decomposed, hydrochloric acid is separated, and a white powder is formed, which is an *oxichloride of tin*, its components being 1 atom of protoxide, 1 of protochloride, and 2 of water. (BERZELIUS.) The protochloride of tin, or *salt of tin* of commerce, is made by putting 1 part of granulated tin into a jar or deep basin upon a sand-heat, and pouring upon it 1 part of hydrochloric acid, so that it may be exposed to the joint action of the acid and air; after some hours 3 parts more of the acid are added, and the mixture stirred and digested till a saturated solution is obtained. During the process, a very fetid hydrogen gas is given off, and the greater part of the tin is dissolved; when the clear liquor is poured off it is set aside to crystallize; the mother-liquors are again evaporated as long as they afford crystals, and the residue is afterwards employed for conversion into bichloride.

In consequence of the decomposition above mentioned, the aqueous solution of protochloride of tin is always turbid, but becomes clear on the addition of hydrochloric acid. This acid solution quickly absorbs oxygen, and if added to certain metallic solutions, revives or deoxidizes them. It decomposes and precipitates sulphur from sulphurous acid. It reduces the persalts of iron to protosalts, and converts arsenic acid into arsenious acid, and chromic acid into oxide of chromium. With a very weak solution of corrosive sublimate it forms a grey precipitate of metallic mercury. Added to a dilute solution of chloride of platinum it changes its color to a deep blood-red. With solution of gold it produces a purple precipitate used in painting porcelain, and known under the name of *Purple of Cassius*. With infusion of cochineal it produces a purple precipitate; and it is much used to fix and change colors in the art of dyeing and calico-printing. The greater number of vegetable infusions are precipitated by

it, in consequence of the insoluble compounds which it forms with the varieties of extractive matter. (On the preparation of this salt see BERRARD, *Ann. de Chim.*, LXviii. 78; and CHAUDET, *Ann. Ch. et Ph.*, iii. 276.) Protochloride of tin consists of

						J. Davy.
Tin	1	59	62.1 62.22
Chlorine	1	36	37.9 37.78
<hr/>						<hr/>
Protochloride of tin.....	1		95		100.0	100.00

AMMONIO-PROTOCHLORIDE OF TIN. 2 atoms of heated protochloride of tin absorb 1 of ammonia. (PERSOZ.) A protochloride of tin and ammonia sublimes in octohedral crystals when a mixture of tin filings and sal-ammoniac is heated, hydrogen and ammonia being at the same time evolved. Their formula is $\text{NH}_4\text{Cl}, \text{SnCl}$: their aqueous solution becomes turbid when boiled. (APJOHN.) Poggiale obtained a salt in permanent fascicular needles $= 2\text{NH}_4\text{Cl}, \text{SnCl} + 5\text{HO}$. He has also described a corresponding potassium salt $= 2\text{KCl}, \text{SnCl} + 3\text{HO}$, in long needles; a prismatic barium salt $= \text{BaCl}, \text{SnCl} + 4\text{HO}$; and an acicular strontium salt $= \text{SrCl}, \text{SnCl} + 4\text{HO}$.

PERCHLORIDE OF TIN. SnCl_2 . If tin be heated in excess of chlorine, or if amalgam of tin be distilled with excess of corrosive sublimate, a *perchloride* is obtained. The best proportions are 6 parts of tin previously combined with 1 of mercury, and intimately mixed with 30 of corrosive sublimate. The mixture is put into a glass retort with a sufficiently capacious receiver luted to it, and may be distilled over a small charcoal fire: the heat should be slowly raised, to prevent too sudden action: towards the end of the process a little of the protochloride rises. Perchloride of tin may also be procured by passing chlorine over the protochloride of tin, or by distilling a mixture of chloride of sodium and persulphate of tin: $2\text{NaCl} + [\text{SnO}_2, 2\text{SO}_3] = 2[\text{NaO}, \text{SO}_3] + \text{SnCl}_2$. It is a transparent colorless fluid, formerly called *Libavius's Fuming Liquor*; it exhales copious fumes when exposed to moist air, and with one-third its weight of water it forms a crystallized hydrate ($= \text{SnCl}, 5\text{HO}$. LEWY.) It does not congeal at -20° . Its boiling-point is 250° ; and, according to Dumas, the density of its vapor is 9.19. (*Ann. Ch. et Ph.*, xxxiii. 285.) It is instantly decomposed by metallic zinc, forming chloride of zinc and a precipitate of metallic tin.

A solution of perchloride of tin much used by dyers is made by dissolving tin in a mixture of 2 measures of hydrochloric acid, 1 of nitric acid, and 1 of water; or by exposing the protochloride to a gentle heat with a small addition of nitric acid. The dyers also prepare this solution by digesting tin filings in single aquafortis, (nitric acid, sp. gr. 1.3,) to each pound of which they add about 2 ounces of common salt or of sal-ammoniac: this compound acid takes up about one-eighth its weight of tin. These solutions are generally known under the names of *nitromuriate* or *oxymuriate of tin*.

Bichloride of tin consists of

						Berzelius.
Tin	1	59	45.04 42.1
Chlorine	2	72	54.96 57.9
<hr/>						<hr/>
Bichloride of tin	1		131		100.00	100.00

AMMONIO-BICHLORIDE OF TIN. $\text{NH}_3, \text{SnCl}_2$. Ammonia is absorbed by anhydrous bichloride of tin; the compound forms a white powder, which may be sublimed without decomposition, and is soluble in water. Perchloride of tin and hydrochlorate of ammonia also combine in single atomic proportions and form a salt which crystallizes in octohedra, permanent in the air, and very soluble in water; its solution reddens litmus and becomes turbid when boiled with excess of water from the formation of stannic hydrate; its concentrated solution (in 3 parts of water at 58° .) may be boiled without change; it converts the red of cochineal to a bright scarlet. The formula of this salt is $\text{HN}_4 \text{Cl}, \text{SnCl}_2$.

POTASSIO-BICHLORIDE OF TIN. $\text{KCl}, \text{SnCl}_2$. When solutions of chloride of potassium and bichloride of tin are mixed in single atomic proportions and evaporated, anhydrous octohedral crystals are obtained. (JACQUELAIN, *Ann. Ch. et Ph.*, lvi. 130.)

SODIO-BICHLORIDE OF TIN may be prepared as the potash salt; it is very soluble and difficultly crystallizable. According to Bolley it contains 1 atom of bichloride of tin and 2 of chloride of sodium; but Lewy represents it by the formula $\text{NaCl}, \text{SnCl}_2 + 5\text{HO}$, and assigns the same quantity of water to the crystallized stanno-chloride of barium, strontium, calcium, and magnesium. (*Ann. Ch. et Ph.*, March, 1846.)

CHLORATE OF TIN. Recently precipitated hydrated protoxide of tin dissolves in aqueous chloric acid: the solution decomposes with detonations and elevation of temperature into hydrated oxide and perchloride of tin, and free chloric acid. (WAECHTER.)

PROTIODIDE OF TIN. SnI . When equivalent proportions of solutions of iodide of potassium and protochloride of tin are mixed, a crystalline deposit of protiodide of tin ensues, of an orange-red color, and sparingly soluble in cold water. When dissolved in boiling water, it is deposited on cooling in brilliant acicular groups. Exposed to air, this compound slightly deliquesces and forms peroxide of tin and hydriodic acid. It forms double salts with certain basic iodides, and in thus combining with the iodides of potassium, sodium, calcium, barium, and strontium, 2 atoms of the protiodide of tin unite to 1 of the basic iodide: but with hydriodate of ammonia it combines in single atomic proportions. (BOULLAY, *Ann. Ch. et Ph.*, xxxiv. 372.) The protiodide of tin is composed of

						Boullay.	
Tin	1	...	59	...	31·89	...	32·01
Iodine	1	...	126	...	68·21	...	67·99
<hr/>			<hr/>		<hr/>		<hr/>
Protiodide of tin	1		185		100·00		100·00

PERIODIDE OF TIN, SnI_2 , is prepared by dissolving in hydriodic acid the hydrate of the peroxide precipitated by alkalis from the bichloride. It crystallizes in yellow crystals of a silky lustre, which are resolved by boiling water into hydriodic acid and peroxide of tin. (TURNER.)

Periodide of tin is also formed by passing the vapor of iodine over heated tin: it then forms a yellow fusible substance. When iodine, tin

filings, and water are mixed together, peroxide of tin and hydriodic acid are formed. Periodide of tin consists of

Tin	1	59	18.97
Iodine	2	252	81.03
<hr/>					
Periodide of tin	1		311		100.00

IODATES OF TIN. Iodic acid and iodate of potassa give white precipitates in aqueous solutions of protochloride and perchloride of tin. (PLEISCHL.) When solution of protochloride of tin is dropped into iodate of soda a white protiodate of tin falls, which, however, in a few minutes becomes discolored from evolution of iodine and formation of perchloride: if, on the other hand, solution of iodate of soda be dropped into protochloride of tin, the white precipitate presently redissolves, forming a yellow solution, and with more of the iodate iodine is set free. (RAMMELSBURG.)

PROTOBROMIDE OF TIN, SnBr , is formed by heating tin in hydrobromic acid gas, or with protobromide of mercury. It resembles the protochloride of tin.

PERBROMIDE OF TIN. Sn,Br_2 . Metallic tin and bromine act energetically on each other: the metal burns, and a white crystallized compound is obtained, readily fusible and volatile, yielding slight vapors in moist air, and dissolving in water.

BROMATES OF TIN. Bromate of potassa gives a yellowish white precipitate in solution of protochloride of tin. Hydrated peroxide of tin is almost insoluble in aqueous bromic acid. (RAMMELSBURG.)

FLUORIDES OF TIN. The solution of protoxide of tin in aqueous hydrofluoric acid, evaporated out of contact of air, yields small white brilliant crystals. Peroxide of tin dissolves in the acid, but deposits a basic salt when the solution is evaporated. The solution, when heated, coagulates like albumen. (BERZELIUS.)

PROTONITRATE OF TIN; SnO,NO_5 ; may be formed by acting upon the metal by dilute nitric acid, or by dissolving the hydrated protoxide in dilute nitric acid; a yellow solution, which will not crystallize, is obtained; exposed to air, it absorbs oxygen, and peroxide of tin precipitates, or, according to Dumas, a hydrate of the protoxide. If evaporated, the oxide falls, and a portion of nitrate of ammonia remains. During the action of the dilute acid upon the tin no gas is evolved; it is therefore evident that water, as well as part of the acid, are in this case decomposed; the results may be thus represented:

Atoms employed.			Atoms obtained.			
8 Tin	{	8 tin	=	{	8 tin	
10 Nitric acid		10 nitrogen			{	8 nitrogen
3 Water.....		53 oxygen.....				48 oxygen
		3 hydrogen				2 nitrogen
			=	{	5 oxygen	
		1 nitrate of ammonia			3 hydrogen	

By dissolving hydrated protoxide of tin in the dilute acid, a protonitrate, free from ammonia, may be obtained.

PERNITRATE OF TIN. The recently precipitated hydrated peroxide of tin dissolves in nitric acid, and forms a colorless solution, which if strong acid be used, will yield crystals. When diluted or heated, the solution becomes turbid; the addition of nitrate of ammonia renders this salt more stable, and probably forms with it a double salt. When strong nitric acid is made to act upon tin, as in the process above-mentioned for the production of the peroxide, none of the metal is retained in solution, and on evaporation nitrate of ammonia only remains.

PROTOSULPHURET OF TIN. SnS . This compound may be procured by heating tin with sulphur; in consequence, however, of the high temperature required for its formation, so much of the sulphur is generally lost, that a mixture of the metal and of the sulphuret is only at first obtained. This mixture may be pulverized, and heated in a retort with its weight of sulphur, in which case the perfect protosulphuret is the result. A hydrated protosulphuret of tin is precipitated when the salts of the protoxide are mixed with solution of sulphuretted hydrogen, or with an alkaline protosulphuret: it is of a brownish-black color, and loses water when heated. Obtained by the first process, sulphuret of tin is a brittle blackish compound of a laminated texture, sp. gr. about 5.0, fusible at a red-heat, and occasionally forming acicular crystals; it dissolves in hydrochloric acid with the evolution of sulphuretted hydrogen. By the action of chlorine even at common temperatures, it is resolved into liquid bichloride of tin, and a crystalline compound of the bichlorides of tin and sulphur. $2\text{SnS} + 8\text{Cl} = \text{SnCl}_2 + \text{SnCl}_2 \cdot 2\text{SCl}_2$. (H. ROSE.) It consists of

						J. Davy.	Bergman.		
Tin	1	...	59	...	78.66	...	78.6	...	80
Sulphur	1	...	16	...	21.34	...	21.4	...	20
<hr/>									
Protosulphuret of tin	1		75		100.00		100.0		100

SESQUISULPHURET OF TIN. Sn_2S_3 . Berzelius obtained this compound by heating the finely-powdered protosulphuret with one-third its weight of sulphur to dull-redness: it is of a yellowish-grey color, metallic lustre, and when digested in hydrochloric acid gives out sulphuretted hydrogen, and leaves a yellow residue of bisulphuret. Gmelin regards this as a mixture of the protosulphuret and persulphuret. According to Berzelius it contains

					Berzelius.		
Tin	2	...	118	...	71·08	...	71
Sulphur.....	3	...	48	...	28·92	...	29
<hr/>							
Sesquisulphuret of tin.....	1		166		100·00		100

BISULPHURET OF TIN. SnS_2 . A mixture of 4 parts of tin filings, 3 of sulphur, and 2 of sal-ammoniac, carefully heated in a covered crucible, yield bisulphuret of tin; sal-ammoniac, hydrosulphuret of ammonia, sulphuretted hydrogen, and sulphur, are evolved during the process. A mixture of 10 parts of protosulphuret of tin, 3 of sal-ammoniac, and 5 of sulphur, yields the same results. In these operations the sal-ammoniac is said to be indispensable, but according to Proust (*Nicholson's Journal*, xiv. 39), when heat is gradually applied to a mixture of flowers of

sulphur and protochloride of tin, "volatile fuming muriate will pass over in considerable quantity, the excess of sulphur will fix about the neck of the retort, and at the bottom will appear a light mass of brilliant mosaic gold, and part spangle the dome of the vessel with gold-colored flowers." Woulfe has given several formulæ for the production of this sulphuret (*Phil. Trans.*, 1771); but the following, taken from the *London New Dispensatory* of 1765, answers best:—Take 12 oz. of tin and amalgamate it with 6 oz. of mercury, reduce it to powder, and mix it with 7 oz. of flowers of sulphur and 6 oz. of sal-ammoniac, and put the whole into a glass matrass placed in a sand heat. Apply a gentle heat till the white fumes abate, then raise the heat to redness, and keep it so for a due time. On cooling and breaking the matrass, the bisulphuret of tin is found at the bottom. (See Woulfe's paper above quoted in the *Philosophical Transactions*, and the article TIN in Aikin's *Chemical Dictionary*.) According to Berzelius, the use of the mercury in these operations is to facilitate the fusion of the tin and its combination with the sulphur, while the sal-ammoniac prevents such increase of temperature as would reduce the tin to the state of protosulphuret.

A hydrated bisulphuret of tin is formed by decomposing a solution of perchloride of tin by sulphuretted hydrogen, avoiding the presence of excess of acid. The precipitate is pale yellow; it becomes of a dingy yellow when dried, and has a vitreous fracture.

The extraordinary golden lustre of the bisulphuret of tin and its flaky texture rendered it an object of great interest to the alchemists: it was termed *aurum musivum*, and *mosaic gold*. When well made it is in very soft golden flakes, very friable and adhering to the fingers, sp. gr. 4·4 to 4·6. It is insoluble in the acids, except in nitrohydrochloric acid; it is soluble in caustic potassa, but not without partial decomposition. It dissolves in sulphuret of sodium, and the concentrated solution yields crystals of a hydrated double sulphuret, the formula of which is $2\text{NaS} + \text{SnS}_2 + 12\text{HO}$. It is much used for ornamental work, under the name of *bronze-powder*, especially by the manufacturers of paper-hangings: it is chiefly imported from Holland and Germany. It consists of

						J. Davy.	Berzelius.
Tin	1	...	59	...	64·84	...	63·6
Sulphur	2	...	32	...	35·16	...	36·4
<hr/>							
Bisulphuret of tin	1		91		100·00		100·0

Tin pyrites is a rare mineral composed of the disulphurets of copper and iron with bisulphuret of tin, $= 2[\text{Fe}_2\text{S}] \text{SnS}_2 + 2[\text{Cu}_2\text{S}] \text{SnS}_2$. There are other analogous compounds in which basic sulphurets are combined with bisulphuret of tin.

HYPOSULPHITES OF TIN. Tin decomposes an aqueous solution of sulphurous acid; sulphur is evolved, which forms sulphuret of tin: the oxide of tin formed, together with another portion of the sulphur and a certain quantity of sulphurous acid, unite and form a soluble hyposulphite (sulphuretted sulphite) which is retained in solution. (FOURCROY.)

SULPHITES OF TIN. A protosulphite is formed by digesting the prot-

oxide in sulphurous acid, or by precipitating protochloride of tin by sulphite of ammonia: boiling water decomposes this salt, and abstracting the acid, leaves protoxide of tin. (BERTHIER.)

SULPHATES OF TIN. When excess of tin is boiled in sulphuric acid, a solution is obtained which deposits white acicular crystals of *protosulphate of tin*. In this process sulphurous acid is evolved, and some sulphur generally set free, arising out of the simultaneous decomposition of the water and the acid; the nascent hydrogen and the sulphuric acid react on each other, reproduce water, and deposit sulphur. Protosulphate of tin is also precipitated by pouring sulphuric acid into protochloride of tin.

When tin is boiled in excess of sulphuric acid, or when recently precipitated peroxide of tin is dissolved in the acid, a *persulphate of tin* is formed, which, however, cannot be brought to crystallize. Dumas observes, that these sulphates of tin probably form double salts with the alkaline sulphates.

Bancroft's tin mordant is made by pouring 3 parts of hydrochloric acid upon 2 of tin filings, and after an hour carefully adding 1.5 parts of oil of vitriol; the tin dissolves, and the mixture is kept upon the sand heat as long as hydrogen is evolved; when cold, the residue is dissolved in water, poured off from the undissolved tin, and so diluted that 8 parts of the solution may contain 1 of tin.

PHOSPHURET OF TIN may be formed by dropping phosphorus into melted tin, or by heating to redness equal parts of tin filings and superphosphate of lime, or phosphate of ammonia. It is of a silvery color, sectile, and somewhat ductile. When its filings are sprinkled upon hot coals the phosphorus burns. Phosphuret of tin contains, according to Pelletier, 14 *per cent.* of phosphorus.

PHOSPHITES OF TIN. A protophosphite is produced, according to Rose, by mixing protochloride of tin with protochloride of phosphorus saturated by ammonia, (*Ann. Ch. et Ph.*, xxxv. 218,) or by precipitating the solution of the protochloride by phosphite of ammonia: it falls as a white powder; its solution in hydrochloric acid reduces many of the metals: its formula is $2\text{SnO}, \text{PO}_3, \text{HO}$. The solution of bichloride of tin gives a white precipitate with phosphite of ammonia $= 2\text{SnO}, \text{PO}_3$. (H. ROSE.)

PHOSPHATES OF TIN. A *protophosphate* is formed by adding solution of phosphate of soda to the protochloride. It is a white powder, not soluble in water, and fuses at a red-heat into an opaque white enamel. The *perphosphate* of tin may also be formed by double decomposition: it resembles the protophosphate.

CARBONATE OF TIN. When carbonate of potassa is added to protochloride of tin, a white precipitate ensues, which, when washed and dried, loses carbonic acid, so that no permanent carbonate appears to exist.

BORATE OF TIN is an insoluble white powder.

FERROCYANIDE OF TIN. Ferrocyanide of potassium produces a white precipitate in solution of protochloride of tin.

ALLOYS OF TIN. With *potassium* and with *sodium* tin forms brilliant white alloys less fusible than tin. The potassium alloy may be formed by heating the metals together till they combine: it is brittle, granular, fusible at a red-heat, oxidizes by exposure to air, and decomposes water rapidly if acidulated. This alloy may also be formed by heating a mixture of 100 parts of oxide of tin, 60 of calcined tartar, and 8 of lamp black. (SERULLAS.) With sodium tin combines at a dull red-heat: the alloy is brittle, and slowly oxidizes by exposure to air: it acts slowly upon water, unless an acid be present. The compounds of tin with the other light metals have not been examined, neither has that which it probably forms with *manganese*. With *iron* it forms combinations which are white, and more or less fusible according to the proportion of iron which they contain. These metals admit to a certain extent of separation by *liquation*; that is, when the alloys are heated up to a temperature short of their fusion the tin runs off, leaving a less fusible alloy, in which iron always predominates. Bergman observed that, on fusing tin and iron these metals had a tendency to form two definite alloys; the one containing 2 of tin and 1 of iron, the other 2 of iron and 1 of tin. Lassaigne has described an alloy of tin and iron = SnFe_3 , formed in an iron retort long used for distilling off the mercury from an amalgam of tin: when freed from adhering tin, it formed brilliant acicular prisms, sp. gr. 8.73, brittle, and fusible at a high red-heat; its powder burned with sparks and smoke in the flame of a candle; it did not rust in moist air, and was not acted upon by nitric acid (?), but slowly soluble in hydrochloric acid, and rapidly in nitrohydrochloric acid. It consisted of

	Lassaigne.						
Tin	1	...	59	...	41.26	...	42.1
Iron	3	...	84	...	58.74	...	57.9
	1		143		100.00		100.0

Tin plate is a most useful alloy of tin and iron, in which iron plate is superficially alloyed with tin, and to the surface of which a quantity of tin further adheres, without being in combination. It is made by dipping the cleansed iron plates into a bath of melted tin; the process is described at length by Parkes. (*Chemical Essays*.) An alloy, composed of 6 parts of tin and 1 of iron, made by fusing tin with iron turnings, is sometimes used as a substitute for pure tin in tinning copper vessels; its specific gravity is 7.247; it is brittle when hot, but somewhat malleable when cold; it fuses at a red-heat. The objection to these combinations generally is, that in consequence of the electrical relations of the two metals, the iron, if anywhere exposed, has an increased tendency to rust and oxidizement. This is especially the case with tin plate; for although the surface of the tin itself is sufficiently durable, no sooner is any portion so abraded as to denude the iron, than a spot of rust appears and rapidly extends: hence the superiority of iron plate covered by zinc instead of tin, zinc being electro-positive, whereas tin is electro-negative in regard to iron, under the influence of common oxidizing agents. (See p. 195, and *note*.)

Moiré metallique is tin plate which has been superficially acted on by an acid so as to display by reflected light the crystalline texture of the tin; the tin plate best suited for the purpose is that which has rather a thick coating of pure tin. It should first be well cleansed by washing its surface with a little caustic potash, then in water, and drying it. The acid employed is always some modification of the nitrohydrochloric more or less diluted; 8 parts of water, 2 of nitric, and 3 of hydrochloric acid generally answers well. The plate should be slightly heated, and then quickly sponged over with the acid, so as to bring out the *moiré*; it should then immediately be dipped into water, well washed and perfectly dried; if the acid has blackened or oxidized the surface, a solution of caustic potash will generally clean it. The crystals on the unprepared tin plate are usually large and indistinct, so that its texture is often modified expressly for the purpose, by heating it up to the point of the fusion of the tin, powdering it over with sal-ammoniac to remove the oxide, and then plunging it into cold water; in this way the crystals are generally small. By sprinkling the surface of the heated plate with water, or by only partially fusing the tin by holding the plate over the flame of a spirit-lamp, or running a blow-pipe flame over it, various modifications of the crystalline surface may be obtained, or different devices sketched as it were upon it. The plates are generally finished by a coating of transparent or colored varnish.

Tin and *zinc* form a hard alloy, stronger than tin, and not brittle. An alloy of equal parts of zinc and tin resists friction, and is almost as tenacious as brass. (KOECHLIN.)

The *tinning of pins* is effected by boiling them for a few minutes in a solution of 1 part of bitartrate of potassa, 2 of alum, and 2 of common salt, in 10 or 12 of water, to which some tin filings or finely granulated tin are added; they soon become coated with a brilliant and adhesive film of tin, and are then taken out, cleaned, and dried. The pins are made of brass wire, and require to be perfectly clean before they are put into the tinning liquor. (See the experiments of Gadolin and Gedda upon the precipitation of tin by copper. *Jour. de Phys.*, xxxiv. 362 and 430.)

Tin medals, or casts in tin, are *bronzed* by being first well cleaned, wiped, and washed over with a solution of 1 part of protosulphate of iron, and 1 of sulphate of copper, in 20 of water: this gives a grey tint to the surface; they are then brushed over with a solution of 4 parts of verdigris in 11 of distilled vinegar; left for an hour to dry; and polished with a soft brush and colcothar.

CHARACTERS OF THE SALTS OF TIN. The salts of the *protoxide* have a highly astringent and disagreeable taste, and are mostly colorless; they are precipitated white by ferrocyanide of potassium; brown or nearly black by hydrosulphurets of the alkalis; white by caustic soda and potassa, and excess of alkali redissolves the precipitate. With ammonia and carbonates of potassa and soda the precipitate is white, and insoluble in excess of the precipitant. They reduce the persalts of many metals to the state of protosalts; such as the persalts of copper, iron, and mercury: with dilute solution of gold they give a red or purple precipitate. Succinates and benzoates of the alkalis give white, and tincture of galls

yellow, precipitates. The salts of the *peroxide* are colorless, and do not reduce the other metallic persalts; heated with nitric acid, peroxide of tin is generally separated: they are precipitated white by ferrocyanide of potassium, and dirty yellow by the hydrosulphuretted alkalis. With soda and potassa they behave as the protoxide; with their carbonates and with caustic ammonia hydrated peroxide of tin is thrown down, slightly soluble in excess of those precipitants.

Protochloride of tin is decomposed by zinc and by cadmium, which quickly and entirely precipitate tin in a metallic state. Lead immersed in a solution of the protochloride of tin becomes covered with spicular crystals of the latter metal, which prevent further action. Pure and anhydrous perchloride of tin is not decomposed by these metals; if water be present it is acted upon as the protochloride. The alkaline solution of oxide of tin is reduced by zinc and cadmium, and less perfectly by lead.

In quantitative analysis tin is almost always weighed as peroxide: thus, in the analysis of alloys of tin they should be boiled in moderately strong nitric acid, the liquid evaporated till the greater part of the acid is expelled, water added, and the insoluble peroxide of tin collected upon a filter, washed, carefully ignited, and weighed. When tin is separated as sulphuret it should also be peroxidized by nitric acid, and weighed in that state.

The analysis of *native oxide of tin* may be performed as follows: (PARNELL.) Reduce the ore to fine powder, mix it with 6 parts of caustic potassa or soda, heat the mixture to dull redness in a covered silver crucible for half an hour, and dissolve the resulting mass in hydrochloric acid: evaporate off most of the excess of acid, dilute the remaining liquid with water, and precipitate the tin as sulphuret by sulphuretted hydrogen, converting it afterwards by nitric acid into *peroxide*. The filtered liquid from the sulphuret contains protochloride of iron; peroxidize it by boiling with nitric acid, neutralise with ammonia, and precipitate peroxide of iron by a neutral benzoate or succinate: from the liquor filtered from this last precipitate, manganese, if present, may be thrown down by hydrosulphuret of ammonia.

§ XII. CADMIUM. Cd. 56.

THIS metal was discovered in 1817, by Professor Stromeyer, of Göttingen, in examining into the cause of the yellow color of certain oxides of zinc, which had been erroneously suspected to contain arsenic; he called it *Cadmium*, from *καδμεια*, a term formerly applied both to calamine, and to the substance which sublimes from the furnace during the manufacture of brass. It is contained in certain ores of zinc, and especially in the *black fibrous blende* of Bohemia. It has been detected by Clarke in the *calamine* of Derbyshire and Somersetshire, and in the zinc of commerce (*Ann. of Phil.*, xv. 272, and New Series, iii. 123), and Herapath found it in considerable proportion in the sublimate which, in the process for obtaining zinc, rises before that metal, forming what the workmen called the *brown blaze*. (*Ann. of Phil.*, iii. 435.)

Cadmium may be procured by digesting the ore in diluted hydrochloric acid, by which a mixed solution of chloride of zinc and cadmium is obtained: it should be evaporated to dryness, to drive off excess of

acid, and re-dissolved in water. Immerse a plate of iron into this solution, to separate all that may be thus precipitated, and afterwards filter the liquor into a platinum capsule, containing a piece of zinc. The cadmium will coat over the surface of the capsule, and adhere so firmly to it, that it may be washed, and thus freed from any remaining solution of zinc. Hydrochloric acid dissolves the precipitate with effervescence, and from this solution it is thrown down white by the alkalis, and yellow by sulphuretted hydrogen. (WOLLASTON.) Oxide of cadmium may be reduced to the metallic state by mixing it with charcoal, and applying a red-heat in a tube or retort, when the cadmium, being volatile at that temperature, sublimes.

Stromeyer separates cadmium from the ores containing it, by digesting them in dilute sulphuric acid, and passing sulphuretted hydrogen through the acidulous solution. He washes the precipitate thus formed, dissolves it in hydrochloric acid, and expels the excess of acid by evaporation. He then redissolves the residue in water, precipitates by carbonate of ammonia, of which an excess is added, for the purpose of retaining the oxides of zinc and copper in solution; the remaining carbonate of cadmium is washed, dried, and heated with lamp-black, by which it is easily reduced.

Cadmium, in its physical properties, much resembles tin, but it is rather harder and more tenacious: it crackles when bent: its specific gravity is 8.60, and somewhat exceeds 8.69 after hammering, (9.05 CHILDREN). It fuses at a temperature a little above that required by tin, and distils over at a heat somewhat below redness, condensing into metallic globules: its vapor is inodorous. Air scarcely acts upon it except when heated, when it forms an orange-colored oxide, not volatile, and easily reducible. Its equivalent is 56. (55.8 TURNER: 55.83 GRAHAM: 56 GMELIN.)

OXIDE OF CADMIUM. CdO . The metal slowly dissolves in dilute sulphuric or hydrochloric acid with the evolution of hydrogen. At a high temperature, sufficient to raise it in vapor, it decomposes water, as when the vapor of cadmium and steam are passed together through a red-hot tube. (REGNAULT, *Ann. Ch. et Ph.*, LXii. 351.) The oxide is best obtained by dissolving the metal in dilute nitric acid, and precipitating it in the state of carbonate, which is then washed, dried, and ignited. It is of a reddish-brown or orange color, (sp. gr. 6.9 KARSTEN; 8.18 HERAPATH): it is neither volatile nor fusible; but when mixed with carbonaceous matter it appears volatile, in consequence of its easy reduction, and the burning off of the separated cadmium. When thrown down from its solutions by alkalis, it forms a white *hydrate*, which absorbs carbonic acid from the atmosphere and is soluble in excess of ammonia, but insoluble in potassa and soda.

Oxide of cadmium consists of

						Stromeyer.
Cadmium	1	...	56	...	87.5	87.45
Oxygen	1	...	8	...	12.5	12.55
<hr/>						<hr/>
Oxide of cadmium	...	1	64		100.0	100.00

CHLORIDE OF CADMIUM. CdCl , is formed by dissolving the hydrated oxide in hydrochloric acid: on evaporation small prismatic crystals are

obtained, very soluble in water, and efflorescent in a dry atmosphere; they readily fuse, and losing water of crystallization, concrete into a transparent lamellar crystalline mass, which is *chloride of cadmium*: at a very high temperature it is volatile, and condenses in the form of a nacreous sublimate. It consists of

						Stromeyer.
Cadmium.....	1	...	56	...	60·9	61·38
Chlorine	1	...	36	...	39·1	38·62
<hr/>						<hr/>
Chloride of cadmium	1		92		100·0	100·00

AMMONIO-CHLORIDE OF CADMIUM. CdCl, NH_3 . If chloride of cadmium be treated with solution of ammonia a white powder is formed, which disappears on the application of heat, and a granular crystalline powder falls out of the solution as it cools, composed as above. If dry ammonia be passed over pulverised anhydrous chloride of cadmium absorption takes place, the chloride increases in bulk, heat is evolved, and the resulting compound is $\text{CdCl}, 3\text{NH}_3$. By exposure to air this white powder loses 2NH_3 , and becomes the former compound. (CROFT, *Mem. Ch. Soc.*, I. 104.) When chloride of cadmium and sal-ammoniac are dissolved together in single atomic equivalents, the concentrated solution first forms acicular crystals containing an atom of water, but these are gradually replaced by anhydrous rhomboids $= \text{NH}_4 \text{Cl}, \text{CdCl}$.

POTASSIO-CHLORIDE OF CADMIUM. CdCl, KCl , is obtained by dissolving the respective salts in atomic proportions; from their concentrated solution the double salt separates in silky needles, which are hydrated, but which gradually disappear, and anhydrous rhombohedrons are subsequently deposited. 100 of water at 60° dissolve 33·45 of the anhydrous salt; it is also soluble in alcohol. (CROFT.)

SODIO-CHLORIDE OF CADMIUM, forms verrucose crystals $= \text{CdCl}, \text{NaCl}, 3\text{HO}$. They are soluble in alcohol, and 100 of water at 60° dissolve 71·32. (CROFT.)

CHLORATE OF CADMIUM, obtained by decomposing sulphate of cadmium by chlorate of baryta, and evaporating over sulphuric acid, gives deliquescent prismatic crystals, $= \text{CdO}, \text{ClO}_5, 2\text{HO}$, soluble in alcohol; they melt at 176° , giving off water, oxygen, and chlorine, and the residue forms a fused grey mass, consisting of oxide and chloride of cadmium.

IODIDE OF CADMIUM. CdI , is a colorless crystallizable compound, fusible, and resolved at a high temperature into iodine and cadmium. It is easily formed by heating filings of cadmium with iodine, or mixing them in a moist state. Its alcoholic or aqueous solution yields large six-sided tables, of a pearly lustre. It consists of

						Stromeyer.
Cadmium	1	...	56	...	30·77	30·541
Iodine	1	...	126	...	69·23	69·459
<hr/>						<hr/>
Iodide of cadmium	1		182		100·00	100·000

AMMONIO-IODIDE OF CADMIUM. A compound $= 3\text{NH}_3, \text{CdI}$, is ob-

tained by gently heating iodide of cadmium in gaseous ammonia: at a higher temperature ammonia is expelled. By dissolving iodide of cadmium in warm aqueous ammonia crystals of $\text{NH}_3\text{,CdI}$ are deposited on cooling. (RAMMELSBERG.)

POTASSIO-IODIDE OF CADMIUM. CdI,KI , is an extremely soluble compound. (CROFT.)

BROMIDE OF CADMIUM. CdBr . Bromine does not act upon cadmium at common temperatures, but when the vapor of bromine is passed over cadmium highly heated in a tube, white vapors are formed, which afterwards condense. When bromine and filings of cadmium are mixed with water, a solution of bromide of cadmium is also obtained.

This compound is very soluble in water, and when its hot saturated solution cools, it deposits white acicular prisms, which effloresce in the air; when heated, these crystals fuse, lose water, and, at a red heat, sublime, yielding nacreous scales. This bromide dissolves in alcohol and ether, and in concentrated acetic and hydrochloric acid, without decomposition; it is also very soluble in ammonia. (BERTHEMOT.) It consists of

						Berthemat.	
Cadmium	1	...	56	...	41·8	...	41·47
Bromine	1	...	78	...	58·2	...	58·53
<hr/>			<hr/>		<hr/>		<hr/>
Bromide of cadmium	1		134		100·0		100·00

AMMONIO-BROMIDE OF CADMIUM. $2\text{NH}_3\text{,CdBr}$, is formed by the action of gaseous ammonia on bromide of cadmium: it is a voluminous white powder. A concentrated aqueous solution of bromide of cadmium supersaturated with ammonia yields crystals $= \text{NH}_3\text{,Br}$. (CROFT.)

POTASSIO-BROMIDE OF CADMIUM. CdBr,KBr , forms an hydrated acicular, and an anhydrous salt, like the double chloride, but is much more soluble in water. (CROFT.)

BROMATE OF CADMIUM. $\text{CdO,BrO}_5\text{,HO}$, is obtained by decomposing bromate of baryta by sulphate of cadmium and evaporating the filtrate in vacuo over oil of vitriol: it forms rhombic prisms soluble in 0·8 water at 60°. When ammonia is added to a concentrated solution of this bromate so as to redissolve the first precipitate, and the liquor evaporated in vacuo over lime, anhydrous crystals are obtained $= 3\text{NH}_3 + 2[\text{CdO,BrO}_5]$ (RAMMELSBERG, *Poggend.*, LV. 74.)

FLUORIDE OF CADMIUM. CdF , is a difficultly soluble compound.

NITRATE OF CADMIUM. $\text{CdO,NO}_5\text{,4H}_2\text{O}$ forms radiated acicular crystals, which are deliquescent, and soluble in alcohol. They consist of

						Stromeyer.	
Oxide of cadmium.....	1	...	64	...	41·56	...	42·15
Nitric acid.....	1	...	54	...	35·06	...	35·78
Water	4	...	36	...	23·38	...	22·07
<hr/>							
Crystallized nitrate of cadmium	1		154		100·00		100·00

SULPHURET OF CADMIUM. CdS , is obtained in the form of a bright yellow powder insoluble in ammonia and in the fixed alkalis, by precipitating the solutions of the metal with sulphuretted hydrogen, or an alkaline sulphuret. It is also formed by heating cadmium, or its oxide, with sulphur, and concretes, on cooling, into a yellow lamellar mass. It dissolves with the evolution of sulphuretted hydrogen in concentrated hydrochloric acid, and is not volatile at a white heat. It furnishes a valuable yellow pigment, which mixes well with other colors, and closely resembles sulphuret of arsenic, from which it is distinguished by sustaining a red-heat without subliming, and by its insolubility in potassa and ammonia. It consists of

						Thomson.	Stromeyer.		
Cadmium	1	...	56	...	77.78	...	77.6	...	78.02
Sulphur	1	...	16	...	22.22	...	22.4	...	21.98
<hr/>									
Sulphuret of cadmium	1		72		100.00		100.0		100.00

NATIVE SULPHURET OF CADMIUM, (*Greenockite*), was discovered by Lord Greenock in small transparent pyramidal crystals of a yellow color, vitreous lustre, and conchoidal fracture, imbedded in prehnite, at Bishopstoun in Renfrewshire: it had been mistaken for a zinc blende, till analyzed by Connell. (*Edin. Phil. Trans.*)

SULPHITE OF CADMIUM. CdO, SO_2 , is formed by dissolving oxide of cadmium in aqueous sulphurous acid. When the metal is digested in this acid, sulphuret of cadmium is at the same time formed, in consequence of the production of sulphuretted hydrogen by the nascent hydrogen which is evolved, $3\text{Cd} + 3\text{HO} + 3\text{SO}_2 = 3[\text{CdO}, \text{SO}_2] + 3\text{H}$; and $3\text{H} + \text{SO}_2 = \text{HS}, 2\text{HO}$; and $3[\text{CdO}, \text{SO}_2] + \text{HS} = 2\text{CdO}, 3\text{SO}_2 + \text{CdS} + \text{HO}$. (GMELIN.)

HYPOSULPHATE OF CADMIUM. $\text{CdO}, \text{S}_2\text{O}_5$, is a very soluble, deliquescent salt. (HEEREN.) When dissolved in warm ammonia it deposits a pulverulent double salt $= 2\text{NH}_3, \text{CdO}, \text{S}_2\text{O}_5$. (RAMMELSBERG.)

SULPHATE OF CADMIUM. $\text{CdO}, \text{SO}_3, 4\text{HO}$, forms transparent prismatic crystals, much resembling those of sulphate of zinc: they are very soluble in water: gently heated, they lose water of crystallization, and at a higher temperature a part of the acid escapes, and a *basic sulphate*, difficultly soluble, and crystallizing in scales, remains. 100 parts of anhydrous sulphate of cadmium absorb 48.69 of ammonia, forming a bulky white powder $= 3\text{NH}_3, \text{CdO}, \text{SO}_3$. (H. ROSE.) The crystals of sulphate of cadmium contain

						Stromeyer.
Oxide of cadmium	1	64	45.72 45.956
Sulphuric acid.....	1	40	28.57 28.523
Water	4	36	25.71 25.521
<hr/>						<hr/>
Crystallized sulphate of cadmium	1		140		100.00	100.000

Sulphate of cadmium forms a double salt with sulphate of potassa $= \text{CdO}, \text{SO}_3$; KO, SO_3 ; 6HO . (MITSCHERLICH.)

PHOSPHURET OF CADMIUM. This is a grey, brittle compound, with a feeble metallic lustre, and very difficult of fusion.

HYPOPHOSPHITE OF CADMIUM. Aqueous hypophosphorous acid saturated with hydrated carbonate of cadmium yields small crystals.

PHOSPHITE OF CADMIUM. Phosphite of ammonia produces a white precipitate in solution of sulphate of cadmium.

PHOSPHATE OF CADMIUM is an insoluble white powder, formed by adding neutral phosphate of soda to a soluble salt of cadmium. It consists, according to Stromeyer, of 69·2 oxide of cadmium, and 30·8 phosphoric acid. It fuses at a high heat into a transparent glass.

CARBONATE OF CADMIUM. CdO, CO_2 , is a white insoluble anhydrous powder, which loses its acid at a red heat, and consists of

						Stromeyer.
Oxide of cadmium	1	64	74·42 74·547
Carbonic acid	1	22	25·58 25·453
<hr/>						<hr/>
Carbonate of cadmium	1		86		100·00	100·000

CYANIDE OF CADMIUM. CdCy , is obtained in anhydrous crystals by evaporating in vacuo a solution of hydrated oxide of cadmium in hydrocyanic acid: it is a very soluble salt. It combines with cyanide of potassium to form a *potassio-cyanide of cadmium*. KCy, CdCy . This double salt is best obtained by evaporating a mixed solution of cyanide of potassium and acetate of cadmium: it forms octohedral crystals soluble in 3 of cold and 1 of boiling water, but insoluble in alcohol. (RAMMELSBERG. *Berzelius' Lehrbuch*.)

BORATE OF CADMIUM is an insoluble white powder, containing, according to Stromeyer, 72·1 oxide, 27·9 acid.

ALLOYS OF CADMIUM. Cadmium combines readily with other metals, forming brittle alloys, from which the cadmium is expelled by a high heat. Those with the antecedent metals have not been examined.

THE SALTS OF CADMIUM are mostly colorless and soluble in water; their solution has a nauseous metallic taste; they are precipitated *white* by caustic and carbonated alkalis, and by ferrocyanide of potassium; and *yellow* by sulphuretted hydrogen and hydrosulphuret of ammonia: they are not affected by tincture of galls. The precipitate by the carbonated alkalis is anhydrous, whereas, with solution of zinc, they throw down a hydrated carbonate; with carbonate of ammonia, the zinc salts give a precipitate soluble in excess of the precipitant; with cadmium salts the precipitate is insoluble. The yellow precipitate which sulphuretted hydrogen occasions in solutions of cadmium has sometimes been mistaken for sulphuret of arsenic; it differs in falling more promptly, in its easy solubility in concentrated hydrochloric acid, its insolubility in ammonia, and its fixity in the fire. Zinc is the only metal which throws down metallic cadmium. The scarcity of cadmium prevents its application to useful purposes, otherwise its malleability would render it available in the arts, and its oxide and sulphuret would be good pigments. Its applications in medicine are probably analogous to those of zinc.

§ XIII. COBALT. Co. 30.

THE following account of the discovery of cobalt is given by Dr. Thomson. (*Inorg. Chem.*, i. 536.) "A mineral called *cobalt**, of a grey color, and very heavy, has been used in different parts of Europe, since the fifteenth century, to tinge glass of a blue color; but the nature of this mineral was altogether unknown till it was examined by Brandt, in 1733. This celebrated Swedish chemist obtained from it a new metal, to which he gave the name of *cobalt*. (*Acta Upsal.*, 1733 and 1742.) Lehmann published a very full account of everything relating to this metal in 1761. (*Cadmialogia, oder Geschichte des Farben-Kobolds*.) Bergman confirmed and extended the discovery of Brandt in different dissertations published in the year 1780. (*Opusc.*, ii. 444, 501, and iv. 371.) Scarcely any further addition was made to our knowledge of this metal till 1798, when a paper on it was published by Tassaert. (*Ann. de Chim.*, xxviii. 101.) In the year 1800, a new set of experiments were made upon it by the School of Mines at Paris, in order to procure it perfectly pure, and to ascertain its properties when in that state. (FOURCROY, *Discours Préliminaire*, p. 114.) In 1802, a new series of trials was published by Thenard, which throw considerable light on its combinations with oxygen. (*Ann. de Chim.*, xlii. 210.) And in 1806, Proust published a set of experiments upon the same subject. (*Ann. de Chim.*, lx. 260.) Considerable attention has been lately paid to the purification of this metal; but hitherto no one seems to have been fortunate enough to hit upon a method altogether free from objections."

The *native* combinations of cobalt are the oxide, and compounds of the metal with iron, nickel, arsenic, and sulphur. It is also found combined with arsenic acid. In the white and grey cobalt-ores, the metal is combined with iron and with arsenic. The ore commonly called *glance cobalt*, from Tunaberg, in Sweden, is a sulpho-arseniuret of cobalt. Some of the varieties are crystallized in cubes, octohedrons, and dodecahedrons. The *red ore* is an arseniate. The finest specimens are the produce of Saxony. Cobalt has also been detected, by Stromeyer, in several speci-

* The word *cobalt* seems to be derived from *Cobalus*, which was the name of a spirit that, according to the superstitious notions of the times, haunted mines, destroyed the labours of the miners, and often gave them a great deal of unnecessary trouble. The miners probably gave this name to the mineral out of joke, because it thwarted them as much as the supposed spirit, by exciting false hopes, and rendering their labour often fruitless; for as it was not known at first to what use the mineral could be applied, it was thrown aside as useless. It was once customary in Germany to introduce into the church-service a prayer that God would preserve miners and their works from *kobalts* and *spirits*. (See BECKMANN'S *History of Inventions*, ii. 362.) Mathesius, in his tenth sermon,

where he speaks of *cadmia fossilis* (probably cobalt ore), says, "Ye miners call it *cobalt*: the Germans call it the black devil and the old devil's whores and hags, old and black *kobel*, which by their witchcraft do injury to people and to their cattle." Lehmann, Paw, Delaval, and several other philosophers, have supposed that *smalt* (oxide of cobalt melted with glass and pounded) was known to the ancients, and used to tinge the beautiful blue glass still visible in some of their works; but we learn from Gmelin, who analyzed some of these pieces of glass, that they owe their *blue* colour, not to the presence of *cobalt*, but of *iron*. According to Lehmann, cobalt ore was first used to tinge glass blue by Christopher Schurer, a glass-maker at Platten, about the year 1540.

mens of meteoric iron. Hydrated peroxide of cobalt is sometimes combined with native peroxide of manganese.

Cobalt is never employed in the metallic state, so that the processes for its reduction are generally carried on upon a small scale, and confined to the experimental laboratory; but there is much difficulty in obtaining pure cobalt: the following are among the best processes for this purpose.

Zaffre, which is a very impure oxide of cobalt, is dissolved in hydrochloric acid by the aid of a little nitric acid, and sulphuretted hydrogen passed through the solution, by which arsenic, copper, (and perhaps other metals,) are precipitated; the filtered liquor may then be boiled with a little nitric acid to peroxidize the iron, and precipitated by carbonate of potassa: the precipitate, when well washed, is to be digested in oxalic acid, which dissolves the oxide of iron and leaves an insoluble oxalate of cobalt; this may be decomposed at a high heat. When dry hydrogen gas is passed over oxide of cobalt, it is also reduced.

The following is Liebig's process for obtaining oxide of cobalt. The ore is pulverized and carefully torrefied; it is then projected by small portions at a time into a crucible or iron vessel, containing 3 parts of bisulphate of potassa, fused by a moderate heat: this mixture, at first fluid, soon acquires a thick pasty consistence; the fire is then raised till the mass is perfectly fused, and white vapors of sulphuric acid no longer emitted. The fused mass contains sulphate of cobalt, neutral sulphate of potassa, perarsenate of iron, and a very little arseniate of cobalt. It is reduced to powder, and boiled (in an iron boiler) with water, to separate the soluble matters; the liquor is then filtered, or decanted clear; (if it contain antimony, bismuth, or copper, these may be separated by sulphuretted hydrogen;) it should be of a rose color, and yields, with solution of carbonate of potassa, a precipitate of carbonate of cobalt. This process is founded upon the permanence of sulphate of cobalt at a red-heat, and the insolubility of the arseniates of iron and nickel in neutral solutions. The oxide thus obtained is free from nickel, and should be so free from iron as not to be discolored by infusion of galls.

Wöhler proceeds as follows: 1 part of pulverized ore (speisscobalt or glance cobalt,) is mixed with 3 parts of carbonate of potassa and 3 of sulphur, in a covered earthen crucible, and fused by a gentle heat, so that the sulphuret of cobalt may not fuse: the product is well edulcorated with water to separate arsenious sulphate of potassium, and subjected to a second similar fusion and edulcoration: it is then digested in nitric acid, to which dilute sulphuric acid has been added, and precipitated by carbonate of soda.

With many cobalt ores the largest part of the arsenic present in the ores of cobalt may be removed by fusing them in fine powder with 3 parts of nitre, and washing out the arseniate of potassa by hot water: the residue boiled in nitric acid leaves some peroxide of iron, and the cobalt is dissolved: the solution, evaporated to expel excess of acid, affords impure nitrate of cobalt, from which copper may be thrown down by a plate of clean iron. The liquor is then filtered, supersaturated by carbonate of ammonia, again filtered from the precipitate of oxide of iron, and evaporated to a small bulk; it is then freed from any deposit, and, evaporated to dryness, leaves tolerably pure oxide of cobalt.

By these processes it often happens that nickel (and sometimes a little

manganese) is contained in the oxide of cobalt, for the removal of which a variety of processes have been suggested. To separate nickel the mixed oxalates of the first process may be dissolved in ammonia, and the diluted solution exposed for several days to air in a shallow basin: the nickel salt falls as a green powder, but the cobalt salt remains in solution: or, when the two oxides are dissolved in excess of nitric acid, the liquor may be supersaturated by ammonia, diluted, and mixed with solution of potassa, by which oxide of nickel is thrown down, and on evaporating the filtered solution the oxide of cobalt falls. This, which is Phillips's process, is effectual; but there is generally some oxide of cobalt carried down with the nickel. (It would here occupy too much space to go into the further details of these and other processes, for which, therefore, I refer to the authorities quoted; to Gmelin's *Handbuch*; to Berzelius's *Lehrbuch*; and to Parnell's *Elements of Analysis*.)

Cobalt is a metal of a reddish-grey color, brittle, and difficultly fusible. Its specific gravity, according to Bergman, is 7.7: according to Turner, 7.834. Tassaert and Lampadius place it at 8.5 and 8.7. The specific heat of a specimen of cobalt not quite pure, as determined by Regnault, was = 0.11712; that of pure cobalt, reduced from the oxalate, being = 0.10696. It is not magnetic when perfectly pure. (FARADAY.) Its equivalent is 30. (29.5 GMELIN and TURNER: 29.57 GRAHAM.)

COBALT AND OXYGEN unite in two proportions, forming oxides corresponding with those of iron, namely, a *protoxide* and a *sesquioxide*: there also appears to be an intermediate oxide, corresponding to the magnetic, or black oxide of iron.

PROTOXIDE OF COBALT, CoO , formed by adding potassa to the nitrate, and washing and drying the precipitate out of contact of air, appears nearly black. By exposure to heat and air it absorbs oxygen, and is converted into *peroxide*. The protoxide, when recently precipitated and moist, is *blue*; if left in contact of water, it becomes a *red hydrate*; it then absorbs oxygen, and acquires a green tint.

The protoxide may also be obtained by heating the carbonate of cobalt out of contact of air; it is then of a greenish-grey color. It is recognised by the facility with which it imparts a blue tint to vitrifiable compounds and to white enamel. It dissolves with the extrication of heat in nitric and sulphuric acid; and is known to be free from peroxide, by dissolving in hydrochloric acid without the evolution of chlorine. When hydrogen is passed over it at a red-heat, it is decomposed, and porous metallic cobalt remains, which is sometimes pyrophoric. It consists of

						Rothoff.	Berthier.
Cobalt	1	30	78.9 78.67 78.75
Oxygen	1	8	21.1 21.33 21.25
<hr/>							
Protoxide of cobalt.....	1		38		100.0	100.00	100.00

PEROXIDE OF COBALT. SESQUIOXIDE OF COBALT. Co_2O_3 . When either the finely-divided metal, or the protoxide, are heated in the air, they absorb oxygen, and acquire a dark-brown color, forming an oxide intermediate between the peroxide and protoxide, and probably of indefi-

nite composition; but according to Hess, (*Poggend.*, xxvi. 542,) consisting of Co_3O_4 . When chlorine is passed through a mixture of the hydrated protoxide and water, or when a solution of chloride of cobalt is decomposed by chloride of lime, a black precipitate falls, which is the *hydrated peroxide*, $\text{Co}_2\text{O}_3, 3\text{H}_2\text{O}$, and which may be deprived of water by very cautious drying at a high temperature; it is then black, and insoluble in dilute acids; it does not form salts; when acted on by hydrochloric acid it evolves chlorine, and yields a protochloride. It sometimes occurs *native*, but is very rare. It consists of

						Rothoff.
Cobalt	2	...	60	...	71.4	71.08
Oxygen	3	...	24	...	28.6	28.92
<hr/>						<hr/>
Sesquioxide of cobalt	1		84		100.0	100.00

CHLORIDE OF COBALT. CoCl . Cobalt, in fine powder, burns when heated in chlorine, and forms *chloride of cobalt*. When cobalt or oxide of cobalt is dissolved in hydrochloric acid, evaporated to dryness, and the residuum heated to redness out of the contact of air, a substance of a blue color and micaceous texture is obtained, which is a pure chloride of cobalt, consisting of

						Brande.
Cobalt	1	...	30	...	45.4	47.75
Chlorine	1	...	36	...	54.6	52.25
<hr/>						<hr/>
Chloride of cobalt ...	1		66		100.0	100.00

When this blue anhydrous chloride of cobalt is dissolved in water it yields a pink solution, which, if duly diluted, and written with, becomes invisible when dry; but if gently heated, the writing appears in brilliant blue, which soon vanishes as the paper cools, in consequence of the salt absorbing aërial moisture; if overheated, the writing blackens, in consequence of the decomposition of the chloride and the paper. This solution has been termed *Hellot's sympathetic ink*. Dr. Thomson states that it was first made known by Waith, in 1705; a second time by Teichmeyer, in 1731; and, lastly, by Hellot, in 1737. (*Mém. Paris.*) If it contain copper, nickel, or iron, the writing appears green; hence, in what are termed *magic landscapes*, the sky is tinted with solution of pure chloride of cobalt, and the trees and grass with that which is cupreous. By careful evaporation, the solution of this chloride forms red crystals, in the form of oblique rhombic prisms, (BROOKE, *Ann. of Phil.*, 2nd Series, vii. 365,) composed of 1 atom of the chloride and 5 of water.

Dumas observes that chloride of cobalt may be obtained by passing chlorine over the finely-powdered ore of cobalt (glance cobalt). The chlorides of arsenic, sulphur, and iron, are volatilized, and the chloride of cobalt remains, provided only a moderate heat has been used.

AMMONIO-CHLORIDE OF COBALT. $2\text{NH}_3, \text{CoCl}$. Anhydrous chloride of cobalt readily absorbs about 34 *per cent.* of gaseous ammonia, forming a bulky pale red powder: with water it gives a red-brown solution, and deposits green hydrated oxide. (H. ROSE.)

CHLORATE OF COBALT. CoO, ClO_5 . By mixing solutions of sulphate of cobalt and chlorate of baryta, filtering, and evaporating over sulphuric

acid, cubic and octohedral crystals are obtained, very deliquescent, soluble in alcohol, fusing at 122° , and decomposed at 212° into chlorine, oxygen, water, and peroxide of cobalt.

IODIDE OF COBALT. CoI . Powdered cobalt heated with iodine in a glass tube, forms a fusible green compound: it is not volatile: dissolved in little water it forms a greenish-brown solution, which becomes red on further dilution: it is soluble in alcohol. (ERDMANN.) Iodide of cobalt absorbs 25 *per cent.* of ammonia, forming a reddish-yellow powder $= 3\text{NH}_3, \text{CoI}$.

IODATE OF COBALT. CoO, IO_5 . The solution of recently-precipitated protocarbonate of cobalt in aqueous iodic acid yields, on cooling, and by evaporation, violet-colored crystalline crusts, which, when heated in a retort to 392° , lose 5.5 *per cent.* of water; and at a red-heat give off iodine and oxygen, and leave an oxide of cobalt $= \text{Co}_3\text{O}_4$, which retains the crystalline form of the iodate: they dissolve in 148 of water at 60° , and in 90 at 212° . (RAMMELSBERG. *Poggend.*, XLIV. 581.)

BROMIDE OF COBALT, CoBr , is formed when cobalt is heated in bromine vapour; it is a green compound, which yields with water a red solution; it becomes purple when concentrated, and reverts to green when dry; it is also formed by boiling powdered cobalt and bromine with water. Anhydrous bromide of cobalt is very deliquescent; it is fusible at a high red-heat, and undergoes slight decomposition. It absorbs 32 *per cent.* of ammonia, forming a reddish-brown powder $= 3\text{NH}_3, \text{CoBr}$. It consists of

						Berthemot.
Cobalt	1	...	30	...	27.7	27.43
Bromine	1	...	78	...	72.3	72.57
<hr/>						
Bromide of cobalt	1		108		100.0	100.00

BROMATE OF COBALT. $\text{CoO}, \text{BrO}_5, 6\text{HO}$. By decomposing protosulphate of cobalt by bromate of baryta, and evaporating the filtrate over oil of vitriol in vacuo, red octohedral crystals are obtained, isomorphous with bromate of magnesia, of zinc, and of nickel: they are soluble in 2.2 cold water, and when the solution is gently heated, oxide of cobalt falls and bromine is evolved. (RAMMELSBERG. *Poggend.*, LV. 71.)

FLUORIDE OF COBALT. CoF . When oxide of cobalt is digested in hydrofluoric acid, a pink solution is obtained, which yields crystals on evaporation, difficultly soluble in water $= \text{CoF}, 2\text{HO}$. When the dilute solution is boiled, it is resolved into a soluble acid salt, and a pale red precipitate, which is an *oxifluoride* $= 2 [\text{CoO}, \text{CoF},] + \text{HO}$. (BERZELIUS.)

NITRATE OF COBALT. CoO, NO_5 . With nitric acid the oxide of cobalt furnishes a brownish-red deliquescent salt in irregular rhombic crystals, consisting, according to Thomson, of $\text{CoO}, \text{NO}_5, 6\text{HO}$. It is soluble in alcohol. It is easily resolved by heat into nitrous acid, oxygen, and peroxide of cobalt. Characters written with it upon paper become pink when warmed, and disappear on cooling, forming a red sympathetic ink.

AMMONIO-NITRATE OF COBALT. When excess of ammonia is added to nitrate of cobalt, part of the oxide is thrown down, and the remainder forms a double salt, which crystallizes in rose-colored cubes of a saline and urinous taste. At a red-heat it fuses like nitrate of ammonia, and leaves peroxide of cobalt. The alkalis do not decompose it, but the sulphurets give a black precipitate. (THENARD. See GMELIN, *Handbuch*, in reference to the properties of this salt.)

AMMONIATED OXIDE OF COBALT. COBALTATE OF AMMONIA. It is doubtful whether any binary compound of ammonia and oxide of cobalt exists. Salts of cobalt with excess of acid are not precipitated by ammonia, nor by ammoniacal salts, because double salts are formed. From a neutral solution of cobalt, ammonia throws down a portion of oxide in the form of blue hydrate, which remains unchanged, provided air be excluded; but, if air has access, oxygen is absorbed, and the precipitate first becomes green, and then dissolves into a brown fluid, which appears to be a compound of *cobaltate of ammonia* with the other ammoniacal salt. L. Gmelin supposes the *cobaltic acid* to consist of 1 equivalent of cobalt and 2 of oxygen; its ammoniacal solution is apt to deposit peroxide of cobalt, in which case it also gives out nitrogen.

PROTOSULPHURET OF COBALT. CoS . When 1 part of carbonate of soda, 2 of sulphur, and 1 of pulverized (native) arsenio-sulphuret of cobalt are heated together, sulphuret of sodium, of arsenic, and of cobalt, are formed, and on cooling, the sulphuret of cobalt separates in bronze-colored scales. When the fused mass is washed, if the ore was pure, sulphuret of cobalt is the only insoluble residue, the double sulphuret of arsenic and sodium being dissolved. (This is probably a sesquisulphuret?) Sulphuret of cobalt may also be obtained by the direct action of sulphur upon cobalt heated to redness. It is also formed by heating sulphate of cobalt with charcoal, but in that case some metallic cobalt is blended with it, for carbon decomposes the sulphuret of cobalt. It is thrown down in the state of hydrate when protosalts of cobalt are decomposed by sulphuretted hydrogen, and the precipitate heated in close vessels loses water and leaves the sulphuret: this is the best process for obtaining the protosulphuret.

Protosulphuret of cobalt is yellowish-grey, somewhat resembling magnetic pyrites in color; it fuses at a red-heat, and is easily soluble in acids. (BERTHIER.) It consists of

Cobalt	1	...	30	...	65.3
Sulphur	1	...	16	...	34.7
<hr/>					
Protosulphuret of cobalt.....	1		46		100.0

Oxysulphuret of cobalt is a dark grey powder, $=\text{CoO},\text{CoS}$, formed when hydrogen is passed over red-heated sulphate of cobalt.

SESQUISULPHURET OF COBALT, Co_2S_3 , is obtained by decomposing sulphate of cobalt by sulphuretted hydrogen at a red-heat, (ARFWEDSON, *Ann. of Phil.*, 2nd Series, vii.) or by passing sulphuretted hydrogen over cobalt below a red-heat. (BERZELIUS.) It is dark grey, and sometimes resembles plumbago. A *native sesquisulphuret of cobalt* is found crystal-

lized and massive: sp. gr. 4·9 to 5 (*Kobaltkies*), of a light steel-grey color, and generally blended with pyrites: it contains cobalt and sulphur in the relative proportions of

						Fellenberg.
Cobalt	2	60	55·5 55·45
Sulphur	3	48	44·5 44·55
<hr/>						<hr/>
Sesquisulphuret of cobalt	1		108		100·0	100·00

BISULPHURET OF COBALT. Co S_2 , was obtained by Setterberg by heating oxide of cobalt with 3 times its weight of sulphur, and treating the product with hydrochloric acid to decompose any protosulphuret, and afterwards with solution of potassa to abstract the excess of sulphur: the bisulphuret remains in the form of a black powder insoluble in hydrochloric acid; it consists of

						Setterberg.
Cobalt	1	30	48·4 47·85
Sulphur	2	32	51·6 52·15
<hr/>						<hr/>
Bisulphuret of cobalt	1		62		100·0	100·00

HYPOSULPHITE OF COBALT, $\text{CoO}, \text{S}_2 \text{O}_2, 6\text{HO}$, was obtained by Rammeisberg by decomposing protosulphate of cobalt by hyposulphite of strontia: on evaporating the filtrate by a gentle heat a red crystalline mass remained.

SULPHITE OF COBALT. When a protosalt of cobalt is boiled with sulphite of potassa, a basic sulphite of cobalt falls. (BERTHIER.)

HYPOSULPHATE OF COBALT, $\text{CoO}, \text{S}_2 \text{O}_5, 6\text{HO}$, forms, according to Heeren, a red saline mass, very soluble, but not deliquescent: he obtained it by the decomposition of sulphate of cobalt by hyposulphate of baryta. The crystals, which are difficultly obtained, contain

Oxide of cobalt	1	38	23·2
Hyposulphuric acid.....	1	72	43·9
Water	6	54	32·9
<hr/>					
Crystallized hyposulphate of cobalt	1		164		100·0

HYPOSULPHATE OF COBALT AND AMMONIA. On mixing a concentrated solution of hyposulphate of cobalt with ammonia, and subsequent warming, a green precipitate and a violet-red liquid are obtained, from which red prismatic crystals are afterwards deposited, but which soon become brown and lose their lustre: with water they yield a pale reddish solution, and deposit a green flocculent precipitate: their formula is $\text{Co}_2 \text{O}_3, 5\text{NH}_3, 2\text{S}_2 \text{O}_5$. (RAMMELSBERG.)

SULPHATE OF COBALT, CoO, SO_3 , forms oblique rhombic prisms, like sulphate of iron (BROOKE, *Ann. of Phil.*, vi. 120, 2nd Series), of a bitterish metallic taste, soluble in 24 parts of water at 60° , and insoluble in alcohol. It may be made by dissolving the newly-precipitated protoxide or carbonate of cobalt in sulphuric acid diluted with its bulk of water, but is not easily crystallized. When dried at a temperature of 500° , the crystals fall into a blue powder, which, in a red-heat, fuses, but does not

give off acid except at a very high temperature. The blue powder is the *anhydrous sulphate of cobalt*, perfectly soluble in water, and forming a pink solution; it is slightly deliquescent, and becomes lilac-colored by exposure to air. Glacial acetic acid throws down the whole of this salt from its aqueous solution. (PERSOZ.) It forms a red sympathetic ink. This salt occurs native. It consists of

						Rothoff.	Brande.		
Oxide of cobalt	1	...	38	...	48·7	...	47·89	...	50
Sulphuric acid.....	1	...	40	...	51·3	...	52·11	...	50
<hr/>									
Anhydrous sulphate of cobalt....	1		78		100·0		100·00		100

The crystals consist of

						Bucholz.	Mitscherlich.	Proust.	
Anhydrous sulphate of cobalt	1	...	78	...	59·1	...	56	...	58
Water	6	...	54	...	40·9	...	44	...	42
<hr/>									
Crystals of sulphate of cobalt	1		132		100·0		100		100

When 1 part of sulphate of cobalt and 2 or 3 of sulphate of zinc are dissolved together and precipitated by carbonate of soda, a precipitate falls, which has been called a cobaltate of zinc; when washed and calcined it acquires a green color, and has been used as a pigment, under the name of *Rinmann's green*.

BISULPHATE OF COBALT is formed by digesting the sulphate in excess of acid; the solution affords long four-sided prismatic efflorescent crystals, composed of 1 atom of protoxide of cobalt, 2 of sulphuric acid, and 3 of water. (THOMSON.) The precipitate which falls from a solution of the sulphate, on the addition of a small quantity of alkali, is a *basic sulphate*. (BERZELIUS.)

AMMONIO-SULPHATE OF COBALT. Sulphate of cobalt forms a double salt with ammonia. If it contain nickel, the crystals are of a greenish tinge, but pink when the cobalt is pure. They are $\text{NH}_4\text{O}, \text{SO}_3 + \text{CoO}, \text{SO}_3 + 6\text{HO}$, being isomorphous with the corresponding salt of magnesia. (MITSCHERLICH.) When anhydrous sulphate of cobalt is exposed to gaseous ammonia, it increases in bulk, heats, and falls into a white powder with a slight tint of red. 100 parts of the salt take up 66·48 of ammonia, forming $3\text{NH}_3, \text{CoO}, \text{SO}_3$. (H. ROSE. *Ann. Ch. et Ph.*, LXii. 313.)

SULPHATE OF COBALT AND POTASSA. $\text{KO}, \text{SO}_3 + \text{CoO}, \text{SO}_3 + 6\text{HO}$. A double salt, isomorphous with the ammonio-magnesian sulphate; it is less soluble, and more easily crystallized than the sulphate of cobalt. (MITSCHERLICH.)

SELENIURET OF COBALT, CoSe , has a grey metallic lustre and foliated fracture: it is fusible at a red heat. (BERZELIUS.)

SELENITE OF COBALT, CoO, SeO_2 , is an insoluble rose-colored powder: the *biselenite* is uncrystallizable. (BERZELIUS.) *Seleniate of cobalt*, $\text{CoO}, \text{SeO}_3, 6\text{HO}$, is isomorphous with the corresponding sulphate. (MITSCHERLICH.)

PHOSPHURET OF COBALT is a white brittle compound, obtained by projecting phosphorus upon red-hot cobalt, or by calcining a mixture of superphosphate of lime, oxide of cobalt, and charcoal; it burns before the blow-pipe, and tarnishes by exposure to air; it contains about 20 *per cent.* of phosphorus. (PELLETIER.) When hydrogen is passed over anhydrous tribasic phosphate of cobalt at a red heat, a black powder is obtained $=\text{Co}_3\text{P}$. (H. ROSE.)

HYPOPHOSPHITE OF COBALT, $\text{CoO}, \text{PO}, 8\text{HO}$, forms, according to Rose, octohedral efflorescent crystals (containing 49.35 *per cent.* of water of crystallization.) According to Wurtz, they lose 6 atoms of water at 212° , and their formula is $\text{CoO}, \text{PH}_2\text{O}_3 + 6\text{HO}$. (*Ann. Ch. et Ph.*, Fevr. 1846.)

PHOSPHITE OF COBALT. CoO, PO_3 . Solution of ammonio-terchloride of phosphorus produces a red precipitate in a solution of protochloride of cobalt: when heated, the precipitate becomes violet, and ultimately black, evolving water and hydrogen. (H. ROSE.)

PHOSPHATE OF COBALT, $3\text{CoO}, \text{PO}_5$, may be formed by double decomposition, as by adding phosphate of soda to chloride of cobalt; it is insoluble in water, of a lilac color, and soluble in excess of phosphoric acid.

Thenard's blue. When phosphate of cobalt is mixed with pure and moist alumina, and exposed to heat, it produces a beautiful blue color, which may sometimes be employed by painters as a substitute for ultramarine: a pure salt of cobalt free from nickel, and pure alumina free from iron, are essential to the production of a fine blue. The alumina and the phosphate are most conveniently mixed when both are recently precipitated and in the hydrated state; 8 parts by bulk of alumina are thus well-mixed with 1 part of the phosphate, and then dried and heated to redness; the crucible is allowed to remain in the fire till the fuel is consumed.

CARBONATE OF COBALT. When the nitrate, chloride, or sulphate of cobalt, are decomposed by carbonate of potassa or soda, a purple powder is precipitated, becoming pink when dried, and readily soluble with effervescence in the acids. Heated in close vessels it gives off carbonic acid, and a grey protoxide of cobalt remains. It dissolves in excess of carbonic acid, and in alkaline carbonates. According to Dumas, the precipitate thrown down from sulphate of cobalt by carbonate of potassa is a sesquicarbonate of cobalt: it is of a rose-color; excess of carbonate of potassa dissolves much of this precipitate, because carbonic acid is set free and produces bicarbonate, in which the carbonate of cobalt is soluble: the solution has a violet tint; by boiling, the whole of the carbonate is thrown down. The carbonate of cobalt which is formed by precipitation with the alkaline bicarbonates, retains its color when dry. According to Setterberg, the precipitate usually called carbonate of cobalt, is, like magnesia alba, a mixture of carbonate and hydrated oxide $= 5\text{CoO}, 2\text{CO}_2, 4\text{HO}$.

AMMONIO-CARBONATE OF COBALT. Carbonate of cobalt is readily soluble in solution of carbonate of ammonia, forming a bright pink

liquid: exposed to air, it deposits small crystals (of protocarbonate of cobalt?)

CYANIDE OF COBALT. CoCy . Hydrocyanic acid, added to acetate of cobalt, throws down the whole of the metal in the form of hydrated cyanide, of a brown color, $= \text{CoCy}, 3\text{HO}$. When anhydrous it is blue, and in close vessels bears a heat of 570° without decomposition: in the air it inflames at 482° . (BERZELIUS.)

FERROCYANIDE OF COBALT. Ferrocyanide of potassium gives a greenish yellow or grey precipitate, and ferridecyanide a brown precipitate, in solutions of cobalt: these precipitates are insoluble in hydrochloric acid.

COBALTOCYANIDE OF POTASSIUM. Cyanide of cobalt is dissolved in a solution of cyanide of potassium; or hydrocyanic acid is added to a solution of cyanide of cobalt, or of carbonate of cobalt, in potassa, till it no longer reddens turmeric; on evaporation, transparent shining prismatic crystals are obtained, which are neutral to vegetable colors, decrepitate when heated, and then fuse into a dark olive-green liquid. This salt is easily soluble in water, and the solution is nearly colorless. The pink precipitate which it produces in the salts of cobalt, is, perhaps, analogous to Prussian blue. (L. GMELIN.) This salt is anhydrous, and consists of

							L. Gmelin.
Potassium	3	...	120	...	35.7	...	35.23
Cobalt	2	...	60	...	17.9	...	17.19
Cyanogen	6	...	156	...	46.4	...	47.58
	<hr/>		<hr/>		<hr/>		<hr/>
	1		336		100.0		100.00

Cobaltocyanogen. When cobaltocyanide of lead is decomposed by sulphuric acid or sulphuretted hydrogen, and the clear solution evaporated, colorless fibrous crystals, acid, deliquescent, and very soluble, are obtained, which when heated, lose water and hydrocyanic acid, leaving a blue residue, which at a red-heat burns into oxide. This compound has been termed *cobaltocyanic acid*; it is supposed to be analogous in constitution to *ferridcyanic acid*, its formula being $\text{Co}_2\text{Cy}_6\text{H}_3$: its basis therefore, or *cobaltocyanogen*, corresponds to ferridcyanogen, and has the formula Co_2Cy_6 : it is a tribasic salt radical, and represented by the symbol Cky , the cobaltocyanic acid being CkyH_3 . "Cobaltocyanide of potassium is obtained by acting on a salt of oxide of cobalt with solution of cyanide of potassium and hydrocyanic acid, when hydrogen is given off, and the new salt is obtained in crystals. The protocyanide of cobalt precipitated on the first addition of cyanide of potassium re-dissolves in excess of that salt, forming either $2\text{CoCy}, \text{KCy}$ or $2\text{CoCy}, 3\text{KCy}$. At all events, there is enough cyanide of potassium present to form the latter compound. The hydrocyanic acid being now added, yields 1 equivalent of cyanogen, converting the 2 equivalents of protocyanide into 1 of sesquicyanide of cobalt, while hydrogen is given off: $2\text{CoCy} + \text{HCy} = \text{Co}_2\text{Cy}_3 + \text{H}$. Lastly, the sesquicyanide, Co_2Cy_3 , with the 3 equivalents of cyanide of potassium, 3KCy , produces the cobaltocyanide of potassium, $\text{K}_3 + \text{Co}_2\text{Cy}_6 = \text{K}_3\text{Cky}$. The crystals are isomorphous with those of the red prussiate of potash (ferridecyanide of potassium:) they are yellow,

and soluble ; their solution is not altered by acids, and gives in solutions of protoxide of cobalt a beautiful rose-colored precipitate, analogous probably to Prussian blue ; possibly, however, it may be CkyCo_3 . It precipitates many other metallic solutions, such as those of lead and silver. It is a singularly permanent salt." (GREGORY.)

SULPHOCYANIDE OF COBALT. Sulphate of cobalt is added to an alcoholic solution of sulphocyanide of potassium ; sulphate of potassa falls, and the blue solution yields prismatic crystals which deliquesce in the air into a liquid, at first violet-colored, then red, and yielding a nearly colorless solution in water, which, on the addition of alcohol, again becomes blue. (GROTHUSS, *Gilbert's Ann.*, lxi. 70.)

MELLONIDE OF COBALT is a pale pink precipitate.

BORATE OF COBALT. Solution of borax occasions a pink precipitate in solution of chloride of cobalt, which is a *borate of cobalt*, and which produces a beautiful blue glass when fused. If fused with 2 parts of phosphate of soda, the product has been recommended as a blue pigment. (BERZELIUS.)

USES OF COBALT. The *alloys of cobalt* are unimportant. The chief use of cobalt is in the state of *oxide* as a coloring material for porcelain, earthenware, and glass ; it is principally imported from Germany in the state of *zaffre*, and *smalt* or *azure*. *Zaffre* is prepared by calcining the ores of cobalt, by which sulphur and arsenic are volatilized, and an impure oxide of cobalt remains, which is mixed with about twice its weight of finely-powdered flints. *Smalt* and *azure blue* are made by fusing *zaffre* with glass, or by calcining a mixture of equal parts of roasted cobalt ore, common potash, and ground flints. In this way a blue glass is formed, which, while hot, is dropped into water, and afterwards reduced to impalpable powder. Thenard's blue is also a valuable pigment, and has lately been much substituted for smalt in the manufacture of paper, though it is said not to be so effectual in covering the original yellow tint of the paper. In consequence of the silica in smalt, writing paper which is blued by it seems to blunt the nibs of pens. There was formerly a large addition of smalt made to bank-note paper, and consequently the ash obtained by the periodical combustion of notes at the Bank often assumed by fusion the appearance of a deep blue vitreous slag : so also the blue-tinted writing-papers leave a fine blue ash when burned, and often exhale an alliaceous odor from the presence of arsenic in the smalt. In paper-making there is some difficulty in keeping the smalt uniformly suspended in the pulp, so that the *lower* side of the sheet is generally bluer than the upper. The manufacturers of paper-hangings also use smalt and Thenard's blue for all brilliant and durable blues.

CHARACTERS OF THE SALTS OF COBALT. Solution of potassa produces a blue precipitate in solutions of cobalt, which becomes green, and if boiled, or long kept, dirty red. It is not redissolved by excess of potassa. Ammonia forms a blue precipitate in solutions of cobalt, which,

on its further addition, becomes green, and mostly dissolves: this solution becomes brown by exposure to air. Carbonate of ammonia produces a pink precipitate, which dissolves in excess of the precipitant, and in hydrochlorate of ammonia. Ferrocyanide of potassium gives a greenish-grey precipitate. Sulphuretted hydrogen does not throw down the metal, but hydrosulphuret of ammonia produces a black precipitate, even when the cobaltic solution is excessively dilute. Those salts of cobalt which are insoluble in water, are nearly all soluble in dilute sulphuric or hydrochloric acid, and are generally thrown down by ammonia, and blackened by hydrosulphuret of ammonia. When no precipitate is produced in an acidulated metallic solution by sulphuretted hydrogen gas, while at the same time a black precipitate is produced in the neutral or alkaline solution, by hydrosulphuret of ammonia, scarcely any other metal than cobalt, nickel, or iron, can be present. (H. ROSE.) Before the blow-pipe, cobalt and its compounds color borax and microcosmic salt blue. By charcoal they are reduced to a grey powder, which is metallic cobalt. (BERZELIUS.) Cobalt is not thrown down in the metallic state by any of the other metals.

§ XIV. NICKEL. Ni. 28.

NICKEL was discovered by Cronstedt, in 1751. Its commonest ore was termed by the German miners, *kupfernickel*, or “false copper:” it is an arsenuret of nickel; it occurs most abundantly in the mines of Saxony and Germany; it has also been found in Dauphiny, Cornwall, and several other localities: there is also a native sulphuret of nickel; what is frequently termed *native nickel* is a variety of the arsenuret.

The common commercial source of nickel is an impure fused arsenuret, known under the name of *Speiss*; it generally contains between 50 and 60 *per cent.* of nickel, and, as has been observed by Wöhler, it occasionally forms octohedral crystals, consisting of 2 atoms of arsenic and 3 of nickel.

An abstract of the numerous processes which have been proposed for obtaining pure nickel will be found in Dumas (*Chim. app. aux Arts*, iii., 253;) in Gmelin's *Handbuch*, (Ed. 1844, III. 332,) and in Berzelius, (*Lehrbuch*, Ed. 1844, II. 656.) It is easily procured *nearly* pure; the difficulty consists in *perfectly* freeing it from all traces of other substances, and especially of cobalt. One of the simplest modes of proceeding is as follows:—Dissolve the impure arsenuret, sold under the name of *speiss*, finely-pulverized, in sulphuric acid diluted with 3 parts of water, by adding the quantity of nitric acid necessary to produce the solution. When cool filter this solution, concentrate it, and set it aside: crystals of sulphate of nickel make their appearance. Proceed in this manner till a sufficient quantity of crystals has been obtained; dissolve and crystallize a second and third time. Then redissolve the purified crystals, and pass sulphuretted hydrogen through the solution, which should be slightly acidulated, to precipitate any copper or arsenic that may be present; boil, filter, and recrystallize. The crystals now obtained furnish a solution from which oxide of nickel is thrown down by potassa: it may, however, still retain cobalt, which is separated by diffusing the hydrated precipitate through water, and subjecting it to a current of

chlorine, by which the cobalt is thrown down (with some nickel) in the form of peroxide, and a solution of chloride of nickel is obtained, from which the pure hydrated oxide of nickel may now be thrown down, by potassa; or, if intended for the production of the metal, by oxalic acid in the state of *oxalate*; which is then dried, and intensely heated in a covered crucible: it affords a button of pure nickel. Nickel may also be obtained by exposing a mixture of lamp-black and the oxide of nickel, made into a paste with oil, to a heat gradually raised to whiteness. The above process is improved by thoroughly roasting the powdered speiss previous to its solution, and by adding to the solution of the first crop of crystals of sulphate of nickel a sufficient quantity of sulphate of potassa, so as to yield, on evaporation, the double sulphate of nickel and potassa: this double salt is then to be treated by sulphuretted hydrogen as above directed.

Wöhler projects a mixture of 1 part of finely-powdered speiss with 2 of nitrate, and 1 of carbonate of potassa, into a red-hot crucible, and then keeps it for some time at a red-heat: on lixiviating the fused mass with water, tolerably pure oxide of nickel remains; it must be dissolved in dilute nitric acid, and if lead, copper, or bismuth be present, these may be thrown down as sulphurets, by a stream of sulphuretted hydrogen; otherwise the solution may at once be precipitated by carbonate of soda and the edulcorated precipitate digested in solution of oxalic acid which forms an insoluble oxalate of nickel, still, however, possibly retaining cobalt, in which case it must be dissolved in excess of ammonia and the solution exposed to air: as the ammonia escapes an insoluble oxalate of nickel and ammonia falls, while the cobalt is retained in solution: the nickel salt, when washed and dried, may be decomposed by a red-heat, and then intensely ignited with charcoal, gives a button of nickel. (See *Cobaltocyanide of Nickel*, in reference to the separation of cobalt from nickel in analysis; also PARNELL'S *Elements of Analysis*, p. 346.)

Nickel is a white brilliant metal, which acts upon the magnetic needle, and is itself capable of becoming a magnet. Its magnetism is more feeble than that of iron, and vanishes at a heat somewhat below redness. (630° FARADAY.) It is nearly as difficult of fusion as iron. It is ductile and malleable: a Bavarian coin has been struck in nickel, and the impression of the die is very perfect. Its specific gravity varies from 8.27 to 8.40 when fused, and after hammering, from 8.69 to 9.00. Its specific heat is 0.10863. It is not oxidized by exposure to air at common temperatures, but when heated in the air it acquires various tints like steel; at a red-heat it becomes coated by a grey oxide: before the oxygen blow-pipe it burns with sparks, somewhat like iron. When steam is passed over nickel at a high red-heat, it is slowly decomposed, and the metal becomes covered with a crystalline green oxide. (REGNAULT, *Ann. Ch. et Ph.*, LXII. 352.) It is very slowly soluble in dilute sulphuric and hydrochloric acid, evolving hydrogen, and producing a protosalt: nitric acid is its best solvent. The atomic weight of nickel deduced from various analyses of its compounds, is between 26 and 30. I have retained 28, as most consistent with the best authorities. (29.5 GMELIN and TURNER, 26 THOMSON.)

PROTOXIDE OF NICKEL, NiO, is obtained by adding potassa to the

solution of the nitrate or sulphate ; a precipitate falls of a pale-green color, which is a *hydrated protoxide*; this, heated to redness, affords a grey protoxide. The carbonate, oxalate, or nitrate of nickel, heated to redness, also afford the protoxide in the form of a grey powder : when intensely heated out of contact of air it becomes green. It is not magnetic. This oxide, in the state of hydrate, easily dissolves in ammonia, forming a sapphire-blue solution ; this property is often made use of to separate oxides of nickel and iron, the latter (peroxide) being insoluble in ammonia. Protoxide of nickel consists of

	Klaproth.				Richter.				Thomson.				Rothoff.			
Nickel.....	1	...	28	...	77.78	...	77	...	77.82	...	78	...	78.55	...	78	...
Oxygen	1	...	8	...	22.22	...	23	...	22.18	...	22	...	21.45	...	22	...
<hr/>																
Protoxide of nickel	1		36		100.00		100		100.00		100		100.00		100	

The hydrated oxide when collected upon a filter is apple-green, and retains its color when boiled in water, and when washed and dried, becoming pulverulent : it may be obtained in crystals by boiling carbonate of nickel in ammonia ; carbonate of ammonia and hydrated oxide of nickel are formed. (TUPPUTI.) It consists of

					Proust.			
Protoxide of nickel	1	...	36	...	80	...	78	
Water	1	...	9	...	20	...	22	
<hr/>								
Hydrated protoxide of nickel....	1		45		100		100	

PEROXIDE OF NICKEL. SESQUIOXIDE OF NICKEL. Ni2 O3. When nitrate or carbonate of nickel are carefully heated nearly to redness, a black powder remains, which is this oxide. It may be obtained as a *hydrate* by passing chlorine through the hydrated protoxide diffused in water, in which case a solution of protochloride is obtained, and the peroxide formed. 3NiO, + Cl = NiCl + Ni2 O3. It may also be formed by the action of a warm solution of chloride of lime upon the hydrated protoxide. When this hydrated oxide is carefully dried, it is = Ni2 O3,3HO. (WINKELBLECH, *Ann. der Pharm.*) Peroxide of nickel is not a salifiable base. It consists of

					Rothoff.				Lassaigne.			
Nickel.....	2	...	56	...	70	...	70.95	...	71.43	...	71.43	
Oxygen	3	...	24	...	30	...	29.05	...	28.57	...	28.57	
<hr/>												
Sesquioxide of nickel.....	1		80		100		100.00		100.00		100.00	

CHLORIDE OF NICKEL. NiCl. When finely-divided nickel is heated in chlorine, the gas is absorbed, the metal burns, and a golden-colored *chloride* results. This compound may also be obtained by dissolving nickel or its oxide in hydrochloric acid, evaporating to dryness, and heating the residue to redness in a glass tube ; it then remains in the form of a yellow lamellar substance, volatile at a high red-heat, which dissolves in hot water, and leaves on evaporation a confusedly crystalline mass, of an apple-green color and sweetish taste = NiCl,9HO. Chloride of nickel consists of

Nickel	1	...	28	...	43.7
Chlorine	1	...	36	...	56.3
<hr/>					
Chloride of nickel	1		64		100.0

AMMONIO-CHLORIDE OF NICKEL. 100 parts of anhydrous chloride of nickel absorb 74.8 of ammonia, becoming a bulky white powder = $3\text{NH}_3, \text{NiCl}$, which yields a blue solution with water. (H. ROSE, *Ann. Ch. et Ph.* LXii. 317.) When alcohol is added to the solution of chloride of nickel in aqueous ammonia, a blue powder falls, and afterwards opaque octohedral crystals, which heated in vacuo decrepitate and fall into a yellow powder, giving out water and ammonia, and leaving chloride of nickel: they are soluble without decomposition in cold water, and insoluble in alcohol: they contain 55.5 per cent. of chloride of nickel. (ERDMANN.) On evaporating a mixed solution of chloride of nickel and sal-ammoniac a green imperfectly crystallized double salt is obtained. (TUPPUTI.)

CHLORATE OF NICKEL. By decomposing chlorate of baryta by sulphate of nickel, and evaporating over sulphuric acid, a dark-green deliquescent salt is obtained in octohedral crystals ($\text{NiO}, \text{ClO}_5, 6\text{HO}$), soluble in alcohol, fusing at 176° , and at 284° beginning to lose water, chlorine, and oxygen: at 342° a black mixture of peroxide and chloride of nickel remains, which at a faint red-heat is converted into a yellow-grey basic chloride, and by long ignition into pure oxide. (WAECHTER.)

IODIDE OF NICKEL. NiI . When very finely divided nickel and iodine are heated together in a glass tube, or when iodine vapor is passed over pulverulent nickel as obtained by the reduction of the oxide by hydrogen, a black compound is produced, from which, when heated to bright redness, iodide of nickel may be sublimed. The solution of oxide of nickel in aqueous hydriodic acid leaves on evaporation a black residue, which when air is excluded sublimes at a red-heat without previous fusion, forming a lamellar iron-colored sublimate: if air be present some oxide is formed and iodine evolved. Iodide of nickel is deliquescent, and forms a brown, or when more dilute, a green solution with water; it is difficultly crystallizable, giving $\text{NiI}, 6\text{HO}$. When large quantities of solution of iodide of nickel are evaporated to dryness, and the residue redissolved, small quantities of a red-brown powder remain = $\text{NiI}, 9\text{NiO}, 15\text{HO}$. (ERDMANN, *Journ. praktisch Chem.*, VII. 254.)

AMMONIO-IODIDE OF NICKEL. $3\text{NH}_3, \text{NiI}$, is obtained by dissolving iodide of nickel in warm caustic ammonia: it separates in blue octohedra, or as a blue powder difficultly soluble in water. Dry iodide of nickel absorbs ammonia, when aided by a gentle heat, forming a yellowish compound = $2\text{NH}_3, \text{NiI}$.

IODATE OF NICKEL. $\text{NiO}, \text{IO}_5, \text{HO}$. Hydrate of oxide of nickel dissolved in aqueous iodic acid yields on evaporation a pale green crystalline powder, which becomes anhydrous when dried at 212° . It is soluble in 120 parts of water at 60° , and in about 78 parts of boiling water. When this iodate is dissolved in aqueous ammonia and alcohol added to the solution, small blue crystals and powder fall = $2\text{NH}_3, \text{NiO}, \text{IO}_5$. (RAMMELSBERG.)

BROMIDE OF NICKEL. NiBr . The vapor of bromine is absorbed by

filings of nickel heated to dull redness, and form a brown compound; when highly heated it assumes the appearance of *aurum musivum*, and at a very high temperature it partly sublimes in yellow micaceous scales, and begins to decompose. This bromide is also formed when nickel and bromine are boiled in water; the solution is green, becomes brown by evaporation, and yields small whitish acicular crystals, very deliquescent, $=\text{NiBr}, 3\text{HO}$. The solution of bromide of nickel exposed to the air, deposits flocks of oxide of nickel: evaporated to dryness a reddish deliquescent bromide remains, soluble in alcohol, ether, hydrochloric acid, and ammonia. At a high red-heat in contact of air it is decomposed, bromine is evolved, and oxide of nickel remains. (BERTHEMOT, *Ann. Ch. et Ph.*, XLIV. 389.)

AMMONIO-BROMIDE OF NICKEL, $3\text{NH}_3, \text{NiBr}$, is formed by saturating the anhydrous bromide with gaseous ammonia, or dissolving it in warm aqueous ammonia, when it separates as a blue powder: it is soluble in a small quantity of water, but when largely diluted is decomposed. (RAMMELSBERG, *Poggend.*, XLIV. 562.)

BROMATE OF NICKEL, NiO, BrO_5 , is obtained by decomposing sulphate of nickel by bromate of baryta and evaporating the filtrate in vacuo over oil of vitriol: it forms octohedral crystals, containing 6HO , soluble in 3.58 cold water. When the concentrated ammoniacal solution of this salt is mixed with alcohol a blue-green crystalline powder falls, which is an *ammonio-bromate*. (RAMMELSBERG.)

FLUORIDE OF NICKEL, obtained by dissolving the hydrated oxide in hydrofluoric acid, yields green irregular crystals, and forms double salts with ammonia and with potassa.

NITRATE OF NICKEL. $\text{NiO}, \text{NO}_5, 5\text{HO}$. Nitric acid acts upon nickel with disengagement of nitric oxide, and a bright green solution of protoxide is obtained, which, by careful evaporation, yields prismatic crystals of protonitrate of nickel: exposed to heat, part of the acid may be driven off so as to leave a green insoluble subnitrate, and this at a higher temperature is decomposed, peroxide, or ultimately protoxide, of nickel remaining. The crystals of nitrate of nickel effloresce in dry air, but deliquesce in a damp atmosphere; they are soluble in 2 parts of water at 60° , and also in alcohol: they consist of

Protoxide of nickel.....	1	36	26.7
Nitric acid	1	54	40.0
Water	5	45	33.3
<hr/>					
Crystallized nitrate of nickel	1		135		100.0

AMMONIA AND OXIDE OF NICKEL. When hydrated oxide of nickel is digested in ammonia it readily dissolves and forms a deep-blue solution, the shade of which is paler when the oxide predominates. When heated, it deposits granular crystals of hydrated oxide: exposed to air, it gradually deposits *ammonio-carbonate of nickel*. The fixed alkalis throw down oxide of nickel, combined with the alkali used.

AMMONIO-NITRATE OF NICKEL. When ammonia is added in excess to nitrate of nickel and the solution evaporated, green crystals of this double salt are obtained: the alkalis do not render their solution turbid, but the hydrosulphurets throw down the nickel. (THENARD, *Ann. de Ch.*, xliii. 245.)

SULPHURET OF NICKEL, NiS, may be formed by heating nickel filings with sulphur; they combine with ignition; also by heating oxide of nickel with sulphur, or by passing sulphuretted hydrogen over the heated oxide. It is yellow, and resembles pyrites. When sulphuretted hydrogen is passed into a perfectly neutral solution of nickel, a part of the metal falls in the form of a black hydrated sulphuret; if the solution be acid, the metal is not thus precipitated: hence the method of separating nickel from certain other metals, such as copper and arsenic, the precipitation of which is not prevented by excess of acid. When acetate of nickel is decomposed by sulphuretted hydrogen, the sulphuret of nickel has a peculiar brilliant metallic lustre. The hydrated sulphuret may be dried at 212° without losing its combined water. A sulphuret of nickel is also thrown down, when the soluble salts of nickel are decomposed by sulphuret of potassium. *Native sulphuret of nickel* occurs in capillary filaments, of a yellow-grey color; it is the *hair pyrites* of the Germans. There is also a native ferrosulphuret, or *nickel pyrites* = Fe₂Ni₃S₃. Sulphuret of nickel consists of

										Rose.	
										<i>Native.</i>	
										Arfwedson.	
										E. Davy.	
Nickel	1	28	63·6	64·35	66	64·8
Sulphur	1	16	36·4	34·26	34	35·2
<hr/>											
Sulphuret of nickel	1		44		100·0		98·61		100		100·0

A *subsulphuret of nickel*, Ni₂S, is formed, according to Arfwedson, when hydrogen is passed over sulphate of nickel at a red heat, sulphurous acid and water being evolved: it is fusible and magnetic. Berthier obtained the same sulphuret by heating sulphate of nickel in a crucible lined with charcoal. By exposing a mixture of carbonate of nickel, sulphur, and carbonate of potassa to a strong heat Fellenberg formed a *bisulphuret of nickel* = NiS₂.

HYPOSULPHITE OF NICKEL. NiO,S₂O₂,6HO. Nickel dissolves like zinc in aqueous sulphurous acid, forming a sulphite and hyposulphite: by evaporating the green solution, crystals of the sulphite first separate, and then those of the hyposulphite. Rammelsberg obtained the hyposulphite by decomposing sulphate of nickel by hyposulphite of strontia, filtering and evaporating the green solution in vacuo over sulphuric acid; it gave green crystals isomorphous with those of hyposulphite of magnesia.

SULPHITE OF NICKEL. NiO,SO₂,6HO. The first crystals deposited by the solution of nickel in sulphurous acid have the above formula. (FORDOS and GÉLIS.)

HYPOSULPHATE OF NICKEL, NiO,S₂O₅,6HO, obtained by the decomposition of sulphate of nickel by hyposulphate of baryta, forms long green prisms, readily soluble in water and decomposed by heat into sulphurous acid and sulphate of nickel.

HYPOSULPHATE OF NICKEL AND AMMONIA. When ammonia is added to a solution of the hyposulphate of nickel a blue crystalline powder falls, which dissolved by the aid of heat in ammonia, forms on cooling small flat prismatic crystals of a violet color. Heated in a tube this salt affords a sublimate of sulphite and sulphate of ammonia, and a residue of sulphuret and sulphate of nickel: its formula is $[3\text{NH}_3, \text{NiO}, \text{S}_2\text{O}_5.]$ (RAMMELSBERG.)

SULPHATE OF NICKEL, $\text{NiO}, \text{SO}_3, 7\text{HO}$, is formed by dissolving the oxide or carbonate of nickel in diluted sulphuric acid: concentrated sulphuric acid acts with difficulty on nickel even at a boiling heat. This salt yields emerald-green prismatic crystals (sp. gr. 2.04), the form of which varies, depending, according to Phillips and Cooper (*Ann. of Phil.*, xxii. 489), upon variations in the water of crystallization; it is soluble in about 3 parts of water at 60° , and efflorescent by exposure; its taste is sweet and astringent; it is insoluble in alcohol and in ether. Exposed to heat, the crystals crumble down into a yellow powder: at a white-heat the acid is expelled, and protoxide remains. They part with 6 atoms of water at 220° , but retain 1 atom till heated to 534° . (GRAHAM.) It has been observed by Mitscherlich, that when the ordinary crystals (containing 7 atoms of water) are exposed in a close glass vessel to the sunshine, or when they are long kept, they become a congeries of small octohedral crystals, which are opaque, but retain the original quantity of combined water. (This salt is sometimes obtained by heating common nickel in sulphuric acid, with the occasional addition of nitric acid; but is impure. See p. 806.) The anhydrous salt consists of

						Berthier.	Tupputi.
Oxide of nickel	1	...	36	...	47.4	47.8	46.6
Sulphuric acid	1	...	40	...	52.6	52.2	53.4
<hr/>							
Anhydrous sulphate of nickel	1		76		100.0	100.0	100.0

The crystallized sulphate consists of

					Tupputi. Mitscherlich. R. Phillips.							
					<i>sq. prism. rhombic p.</i>							
Oxide of nickel	1	...	36	...	25.9	...	25.63	54.4	...	26.2	...	26.30
Sulphuric acid	1	...	40	...	28.8	...	29.37		...	30.0	...	28.16
Water	7	...	63	...	45.3	...	45.00		45.6	...	43.8	...
<hr/>												
Crystals of sulphate of nickel	1		139		100.0		100.00	100.0		100.0		100.00

SULPHATE OF AMMONIA AND NICKEL, $\text{NH}_4\text{O}, \text{NiO}, 2\text{SO}_3, 7\text{HO}$, is obtained by evaporating a mixed solution of sulphate of ammonia and sulphate of nickel; it forms four-sided prismatic crystals (sp. gr. 1.8), of a blue-green color, soluble in 4 parts of cold water, and consisting, according to Mitscherlich, of 1 atom of sulphate of ammonia, 1 of sulphate of nickel, and 8 of water. Boettger recommends this as the best salt for the deposition of nickel upon brass or copper in electro-plating.

Anhydrous sulphate of nickel greedily absorbs gaseous ammonia, evolving much heat and forming a bulky white or pale blue powder, which gives a blue solution in water, and deposits green hydrated oxide: the amount of ammonia absorbed is about 66 per cent., so that the compound may be represented as $3\text{NH}_3, \text{NiO}, \text{SO}_3$. (H. ROSE, *Ann. Ch. et Ph.*, Lxxii. 312.)

SULPHATE OF POTASSA AND NICKEL, $\text{KO}, \text{NiO}, 2\text{SO}_3, 6\text{HO}$, is obtained by mixing and evaporating the mixed solution of sulphate of nickel and sulphate of potassa; or by saturating a solution of bisulphate of potassa with carbonate or oxide of nickel. It forms pale green rhomboidal crystals, (BROOKE, *Ann. of Phil.*, vi. 438,) isomorphous with the corresponding magnesian salt, of a sweetish and bitter taste, soluble in 9 parts of cold water. (TUPPUTI, *Ann. de Chim.*, LXXVIII. and LXXIX.) It has been analyzed by Mitscherlich, and by Cooper (*Ann. of Phil.*, vi. 440), and consists of

						Mitscherlich.	Cooper.
Potassa	1	...	48	...	22.0	21.58	20.48
Oxide of nickel	1	...	36	...	16.5	17.10	17.54
Sulphuric acid	2	...	80	...	36.7	36.63	37.90
Water	6	...	54	...	24.8	24.69	24.08
<hr/>							
Sulphate of potassa and nickel	1		218		100.0	100.00	100.00

SULPHATE OF NICKEL AND IRON is formed by mixing the solution of the two sulphates, or by dissolving the mixed protoxides in sulphuric acid, and evaporating the solution. It is a green efflorescent salt, in tabular crystals. (LINK, *Crell's Ann.*, 1796.)

SULPHATE OF NICKEL AND ZINC is formed by mixing atomic proportions of the two sulphates in solution and evaporating: it forms prismatic crystals of a pale green color, soluble in 3 parts of water at 60° , and efflorescent. (TUPPUTI.)

SELENIURET OF NICKEL has not been examined. *Selenite of Nickel* is a white insoluble powder whilst moist, but becomes pale green when dried. The *biselenite* is soluble, and yields a green gum-like residue on evaporation. The crystals of *seleniate of nickel* are isomorphous with those of seleniate of zinc, and sulphate of nickel. (MITSCHERLICH.)

PHOSPHURET OF NICKEL is a brittle whitish compound, decomposed by exposure to heat and air. It is formed by the action of phosphorus upon red-hot nickel, and is more fusible than the pure metal. It contains, according to Pelletier, 83 nickel + 17 phosphorus; according to Lampadius, 87 nickel + 13 phosphorus. When phosphuretted hydrogen is passed over heated chloride of nickel, or when tribasic phosphate of nickel is heated in a stream of hydrogen, a black phosphuret results = Ni_3P . It is insoluble in hydrochloric, but soluble in and decomposed by nitric acid. (H. ROSE.)

HYPOPHOSPHITE OF NICKEL is a green salt, formed as the corresponding cobalt salt: its formula is $\text{NiO}, \text{PO}, 8\text{HO}$. (WURTZ.)

PHOSPHITE OF NICKEL. A solution of ammonio-terchloride of phosphorus added to a neutral chloride of nickel deposits micaceous crystals, which, when heated, evolve water and hydrogen. (H. ROSE, *Poggend.*)

PHOSPHATE OF NICKEL, $3\text{NiO}, \text{PO}_5$, being nearly insoluble, is preci-

pitated upon adding phosphate of soda to a solution of nickel. It is of a pale-green color, and sometimes forms a crystalline powder. When its solution in ammonia is boiled, a double salt falls.

CARBURET OF NICKEL occasionally remains in the form of a shining powder, when a button of the metal which has long been fused in the contact of carbon, is dissolved in nitric acid. (ROSS and IRVING, *Ann. of Phil.* ii.)

CARBONATE OF NICKEL, NiO, CO_2 , is precipitated in the form of a green powder, when carbonate of soda is added to sulphate of nickel. When long washed with boiling water it becomes nearly black. Dried in the air at the temperature of 60° , it retains its green color. It dissolves in excess of carbonic acid. It has been analyzed by Thomson and by Berthier, its components when dried at 60° being

Oxide of nickel	1	36	43.9
Carbonic acid	1	22	26.8
Water	3	27	29.3
<hr/>					
Carbonate of nickel.....	1		85		100.0

According to Berthier a hydrated sesquicarbonate of nickel, $= 2\text{NiO}, 3\text{CO}_2, 10\text{HO}$, is formed when a salt of nickel is decomposed by bicarbonate of soda: it is a very light greenish powder, not altered by careful desiccation.

AMMONIO-CARBONATE OF NICKEL. Carbonate of nickel forms a blue-green solution with carbonate of ammonia: if a solution of oxide of nickel in ammonia be exposed to air a green basic ammonio-carbonate is gradually deposited.

BORATE OF NICKEL is a pale-green insoluble compound, formed by double decomposition: it is soluble in the stronger acids, and fuses into a hyacinthine glass.

CYANIDE OF NICKEL, NiCy , is thrown down when a soluble cyanide is added to a solution of nickel, or when hydrocyanic acid is mixed with acetate of nickel. When dried it forms a green mass with vitreous fracture, and in this state contains about 20 *per cent.* of water, which it retains till heated to about 380° , when a pale brown anhydrous cyanide remains, which at a higher temperature in close vessels suddenly ignites, evolving nitrogen and cyanogen, and leaving a mixture of nickel and carburet of nickel.

POTASSIO-CYANIDE OF NICKEL. KCy, NiCy . When freshly precipitated cyanide of nickel is dissolved in a solution of cyanide of potassium, yellow rhombic prisms are obtained on evaporation, which are this double cyanide with 1 atom of water: dried at 212° they become anhydrous and opaque, and when fused concrete into a crystalline mass which is slowly decomposed by elevation of temperature. Similarly constituted salts may be obtained with the cyanides of ammonium, calcium, and barium. (WÖHLER.)

FERROCYANIDE OF NICKEL, $2\text{NiCy}, \text{FeCy}$, is precipitated in the form of a pale greenish or grey powder when solution of ferrocyanide of potassium is added to the soluble salts of nickel: the ammoniacal compounds of nickel are similarly precipitated, and in these solutions the test is very distinctive of nickel as opposed to copper.

SULPHOCYANIDE OF NICKEL. Hydrated oxide of nickel dissolves in aqueous hydrosulphocyanic acid, forming a green solution which, evaporated in vacuo, leaves a yellow crystalline powder containing about 5 *per cent.* of water, which it loses at 300° . It is soluble in alcohol, and forms a double salt with ammonia.

COBALTOCYANIDE OF NICKEL, Ni_3Cky , or $\text{Ni}_3\text{Co}_2\text{Cy}_6$. Cobaltocyanide of potassium forms a green precipitate with the salts of nickel, which is insoluble in boiling dilute acids. "This property has been applied by Liebig to the separation of cobalt from nickel in analysis. All other metals being removed, an excess of potash is first added, and then hydrocyanic acid till the precipitate at first formed is dissolved, and the whole is then boiled. Hydrochloric acid is now added, and if no nickel be present it produces no change, because it has no action on cobaltocyanide of potassium. But if nickel be present (of course by this time as cyanide) it is converted into chloride, and this is instantly precipitated by the cobaltocyanide of potassium as cobaltocyanide of nickel. Should there be more cobalt than nickel present, the whole nickel is precipitated, and the precipitate, acted on by potash, leaves the nickel as peroxide, while the cobalt is dissolved as cobaltocyanide and may be determined along with the portion not precipitated for want of nickel. If on the other hand there be more nickel than cobalt, all the cobalt is contained in the green precipitate of cobaltocyanide of nickel, and may be dissolved by potash, and its quantity determined, while the nickel, left by the potash as peroxide, may be added to that left in the liquid for want of cobalt. Such is an outline of this very beautiful and refined method, which gives most accurate results." (GREGORY.)

ALLOYS OF NICKEL. Of these alloys, there is one which requires particular notice, namely, that with *iron*, which forms a principal metallic ingredient in most *aërolites*, or *meteoric stones*. Though we really know nothing of the source or origin of these bodies, it has been ascertained upon satisfactory evidence, that they are not of terrestrial formation; and, consequently, their visits to the surface of our planet have awakened much speculation, and some experimental research.

In the first place, it deserves to be remarked, that we have evidence of the falling of stony bodies from the atmosphere in various countries, and at very remote periods. Such events have been recorded by the most accredited of the early historians. The first tolerably accurate narration of the fall of a meteoric stone relates to that of Ensisheim, near Basle, upon the Rhine. The account, which is deposited in the church, runs thus: "A.D. 1492, Wednesday, November 7, there was a loud clap of thunder, and a child saw a stone fall from heaven: it struck into a field of wheat and did no harm, but made a hole there. The noise it made was heard at Lucerne, Villing, and other places: on the Monday, King

Maximilian ordered the stone to be brought to the castle, and after having conversed about it with the noblemen, said the people of Ensisheim should hang it up in their church, and his Royal Excellency strictly forbade anybody to take anything from it. His Excellency, however, took two pieces himself, and sent another to Duke Sigismund of Austria. This stone weighed 255 lbs."

In 1627, 27th November, Gassendi saw a burning stone fall on Mount Vaisir, in Provence: he found it to weigh 59 lbs. In 1672, a stone fell near Verona, weighing 300 lbs. Lucas, when in Larissa, in 1706, describes the falling of a stone, with a loud hissing noise, and smelling of sulphur. In September, 1753, De Lalande witnessed this phenomenon near Pont de Vesle. In 1768, no less than three stones fell in different parts of France. In 1790, there was a shower of stones near Agen, witnessed by Darcet, and several other persons. On the 13th of December, 1795, a stone fell near Major Topham's house, in Yorkshire; it was seen by a ploughman and two other persons, who immediately dug it out of the hole it had buried itself in: it weighed 56 lbs. We have various other and equally satisfactory accounts of the same kind. All concur in describing a luminous meteor, moving through the air in a more or less oblique direction, attended by a hissing noise, and the fall of stony or semimetallic masses, in a heated state. We have, however, evidence, of another kind, proving the peculiar origin of these bodies. It is, that although they have fallen in very different countries, and at distant periods, when submitted to chemical analysis, they agree in component parts; the metallic particles being composed chiefly of iron and nickel: the earthy of silica and magnesia.

Large masses of *native iron* have been found in different parts of the world, of the history and origin of which nothing very accurate is known. Such are the great block of iron formerly at Elbogen, in Bohemia; the large mass discovered by Pallas, weighing 1600 lbs., near Krasnorjark, in Siberia; that found by Goldberry, in the great desert of Zara, in Africa; probably, also, that mentioned by Barrow, on the banks of the Great Fish-river in Southern Africa; and those noticed by Celis, Humboldt, and others in America, of enormous magnitude, some exceeding 30 tons in weight. That these should be of the same source as the other meteoric stones, seems at first incredible; but when they are submitted to analysis, and the iron they contain found alloyed with nickel, it no longer seems credulous to regard them as of meteoric origin. We find nothing of the kind in the earth. Two blocks of such iron were, in fact, observed to fall from a meteor, at Hradschina, near Agram, in Croatia, in 1751. In URE's *Chemical Dictionary* there is a chronological list of meteoric stones. (Art. METEOROLITE.) See also *Annals of Philosophy*, N.S., vol. xii., p. 83.

To account for these visitations of metallic and lapideous bodies, a variety of hypotheses have been suggested.

Are they merely earthy matter, fused by lightning? Are they the offspring of any terrestrial volcano? These were once favorite notions; but we know of no instance in which similar bodies have in that way been produced, nor do the lavas of known volcanos in the least resemble these bodies; to say nothing of the inexplicable projectile force that would here be wanted. Those who have taken up this conjecture, have

assumed one impossibility to account for what they conceive to be another, namely, that the stony bodies should come from any other source than our own globe.

The notion that these bodies come from the moon, is, when impartially considered, neither absurd nor impossible, for any power which would move a body 6000 feet in a second, that is, about three times the velocity of a cannon-ball, would throw it from the sphere of the moon's attraction into that of our earth. The cause of this projectile force may be a volcano, and if thus impelled, the body would reach us in about two days, and enter our atmosphere with a velocity of about 25,000 feet in a second. Their ignition may be accounted for, either by supposing the heat generated by their motion in our atmosphere sufficient to ignite them, or by considering them combustible, and ignited by contact of air.

While we are stating the *possibility* of these opinions, it may be remembered, that, in the great laboratory of the atmosphere, chemical changes *may* happen, attended by the *production* of metals, though this is highly improbable: the disruption of small planetary bodies is a more plausible hypothesis.

Meteoric stones have generally an uneven black surface, and are internally of a grey color and coarse texture. When carefully examined, most of them appear made up of a number of small spherical bodies and metallic grains imbedded in a softer matter, composed, according to Howard (*Phil. Trans.*, 1802), of silica, magnesia, and iron, with a little nickel; the spherical bodies are nearly of similar composition; and the metallic grains are partly *meteoric iron*, and partly the same with a little sulphur. In addition to these substances, Vauquelin found 2 *per cent.*, of chromium in a stone which fell at Langres, in 1815; (*Ann. Ch. et Ph.*, i. 52:) and Stromeyer detected cobalt in the meteoric iron from the Cape of Good Hope. (*Thomson's Annals*, ix.) Lime and alumina have also been found in them, and a small proportion of manganese. Laugier has announced the existence of a meteoric stone without nickel, but containing chromium; and as he has detected the latter metal in all the *aërolites* which he has examined, he considers it as their most characteristic ingredient. (*Mém. du Muséum*, vi., p. 233.) Dr. Shepard has announced the existence of phosphate of lime in a meteoric stone from Richmond, U.S. (*Silliman's Journ.*, July, 1843.)

In meteoric iron the proportion of nickel varies considerably. In a specimen from the Arctic region I found 3·2 *per cent.* (*Quart. Journ.*, vi. 369.) In that from Siberia, Children found nearly 10 *per cent.* The analysis may be performed by solution in nitrohydrochloric acid; the iron is thrown down by excess of ammonia in the state of peroxide; it is separated by filtration, washed and dried; and on evaporating the filtrated liquor, and heating its dry residue red-hot, the oxide of nickel is obtained, which should be redissolved in nitric acid, and precipitated by pure potassa, the mixture being boiled for a few seconds, (CHILDREN, *Quart. Journ.*, ix. 344); or the nitrohydrochloric solution may be precipitated by excess of ammonia, and filtered: the peroxide of iron remains upon the filter, and the filtrate is an ammoniacal solution of nickel, from which the metal may be precipitated by ferrocyanide of potassium. The following are some further analyses of native iron. (THOMSON'S *Mineralogy*, i. 432. See also BRAYLEY.)

	Klaproth.				M. de Rivero and Boussingault.			
	Selavonia.		Siberia.		From the Andes.			
Iron	96·5	98·5	91·51	91·23 91·76
Nickel	3·5	1·5	8·59	8·21 6·36
	<hr/>		<hr/>		<hr/>		<hr/>	
	100·0		100·0		100·10		99·44	
							98·12	
							98·63	

Meteoric iron has been imitated by fusing iron with nickel. The alloy of 90 iron with 10 nickel is of a whitish-yellow cast, and not so malleable as pure iron. The alloy with 3 *per cent.* of nickel is perfectly malleable, and whiter than iron. These alloys are less disposed to rust than pure iron, but nickel alloyed with steel increases the tendency to rust. (STODART and FARADAY, *Quart. Journ. of Science and Arts*, ix.)

Nothing is known of the alloys of nickel with *potassium*, *sodium*, *manganese*, *zinc*, or *tin*. With *copper*, it forms a hard white alloy; the *white copper* of the Chinese, or *Pakfong*, consists, according to the analysis of Dr. Fyfe, of 40·4 parts of copper, 31·6 of nickel, 25·4 of zinc, and 2·6 of iron. A similar alloy is often used as a substitute for silver, or for plated articles, under the name of *German silver*: it should consist of 1 part of nickel, 1 of zinc, and 2 of copper; or, when intended for *rolling*, of 25 parts of nickel, 20 of zinc, and 60 of copper; to which, if for *casting*, 3 of lead may be added. (GERSDORF, *Quart. Journ.*, i., 1827, 483.) The following details respecting the alloys of nickel are from a pamphlet on the subject by Messrs. Topping. (London, 1836.) The metals referred to should be as pure as possible. (1.) *Common German Silver*.—Copper 8, Nickel 2, Zinc $3\frac{1}{2}$. This is the commonest that can be made, with any regard to the quality of the article produced, and may be used for wire, for common purposes. If the quantity of the nickel be reduced much below this, the alloy will be little better than pale brass, and tarnish rapidly. (2.) *Good German Silver*.—Copper 8, Nickel 3, Zinc $3\frac{1}{2}$. This is a very beautiful compound. It has the appearance of silver a little below standard; by some persons it is even preferred to the more expensive compounds. We strongly recommend manufacturers not to use a metal inferior to this. (3.) *Electrum*.—Copper 8, Nickel 4, Zinc $3\frac{1}{2}$. This is the compound we first introduced. We still prefer it to any of the others, and we think the public in general would do the same. It has a shade of blue, like very highly-polished silver: it tarnishes less easily than silver. (4.) Copper 8, Nickel 6, Zinc $3\frac{1}{2}$. This is the richest in nickel that can be made, without injuring the mechanical properties of the metal. It is a very beautiful compound, but requires a higher heat for fusion than the preceding, and will be found rather more difficult to work. (5.) *Tutenag*.—Copper 8, Nickel 3, Zinc $6\frac{1}{2}$. These proportions we originally obtained by analyzing a piece of Chinese *tutenag*, of the best ordinary quality; but have seen some rare specimens of Chinese *tutenag* equal to *electrum*, No. 3. This alloy is very fusible, but very hard, and not easily rolled: it is best adapted for casting. A variety of articles are now plated with nickel by electrolytic precipitation from a solution of sulphate of nickel, the process being in all respects similar to that in which copper is used (p. 220). [In reference to *electroplating* with nickel, see SMEE, *Elements of Electro-metallurgy*: he recommends chloride of nickel as the solution, with a

nickel positive pole, and single battery: the nickel thus deposited is very brilliant, but rather brittle.]

CHARACTERS OF THE SALTS OF NICKEL. These salts have a rough metallic taste, and excite vomiting when swallowed in sufficient quantity. They are recognized by the peculiar green color of their aqueous solutions, by the green precipitate which they afford with the fixed alkalis and their carbonates, and by giving a green precipitate with ammonia, soluble in excess of that alkali, when it assumes a blue color. The yellow-green precipitate afforded by iodide of potassium, is very characteristic of nickel; but the nicest test of its presence is the ferrocyanide of potassium, which produces a pale-grey or greenish-white precipitate in all the neutral solutions of the metal. To detect the presence of nickel in iron, Wollaston recommends that a small portion, which need not exceed $\cdot 01$ of a grain, should be filed from the sample, and dissolved in a drop of nitric acid; evaporate this to dryness, and add a drop or two of liquid ammonia, which, when gently warmed, will dissolve any oxide of nickel that may be present. The transparent part of the fluid is then to be conducted by the end of a glass rod to a small distance from the precipitated oxide of iron, and mixed with a drop of the ferrocyanide, which, if nickel be present, will cause an immediate milkiness, not discernible when a solution of common iron is formed and treated in the same way. It must, however, be recollected in using this test, that the ferrocyanide precipitate is taken up by excess of ammonia, giving a reddish solution, which, as the ammonia evaporates, forms a flocculent deposit of a buff tinge. Nickel is not precipitated in a metallic form by any metal except iron, which is slow and imperfect in its operation. Zinc, immersed in a solution of chloride of nickel, becomes covered with a suboxide, or a mixture of the metal and its protoxide. The acid solutions of nickel are not precipitated by sulphuretted hydrogen, nor by ammonia; but excess of the latter renders them blue. The alkaline sulphurets give black precipitates of hydrated sulphuret of nickel, which is slightly soluble in excess of those precipitants. Nickel has a great tendency to form double salts, which are only partially decomposed by the alkalis.

Before the blow-pipe oxide of nickel becomes black at the extremity of the exterior flame, and in the interior greenish-grey. It is dissolved readily, and in large quantity, by microcosmic salt. The glass, while hot, is a dirty dark-red, which becomes paler and yellowish as it cools. After the glass has cooled, it requires a large addition of the oxide to produce a distinct change of color. It is nearly the same in the exterior and interior flame, being slightly reddish in the latter. Nitre added to the bead makes it froth, and it becomes red-brown at first, and afterwards paler. It is easily fusible with borax, and the color resembles the preceding. When this glass is long exposed to a high degree of heat in the interior flame, it passes from reddish to blackish and opaque, then blackish-grey and transparent; then paler reddish-grey and clearer; and lastly, transparent, and the metal is precipitated in small white metallic globules. The red color seems here to be produced by the entire fusion or solution of the oxide, the black by incipient reduction, and the grey by the minute metallic particles before they combine and form small globules. When a little soda is added to the glass formed with borax, the reduction

is more easily effected, and the metal collects itself into one single globule. When this oxide contains iron, the glass retains its own color while hot, but assumes that of the iron as it cools.

§ XV. COPPER. Cu. 32.

COPPER, *Cuprum*, or *Venus*, of the alchemists (♀), was known in the early ages of the world, and was the principal ingredient in domestic utensils, and in the instruments of war, previous to the discovery of malleable iron. The word *copper* is derived from the island of *Cyprus*, where it was first wrought by the Greeks. It is found *native*, and in various states of combination. Of its *ores*, the oxide, chloride, sulphuret, sulphate, phosphate, carbonate, and arseniate, are the most remarkable. The sulphurets are the most abundant, and from them the commercial demands are almost exclusively supplied.

The metal may be obtained perfectly pure by dissolving the copper of commerce in nitric acid, with the addition of a little sulphuric acid; the solution is diluted, and a plate of iron is immersed, upon which the copper is precipitated; after having been previously washed in dilute sulphuric acid to separate a little adhering iron, it may be fused into a button. The usual impurities in ordinary copper are traces of lead, iron, oxide of copper, and carbon.

Copper, with the exception of titanium, is the only metal which has a red color: it has much lustre, is very malleable, ductile, and tenacious: it exhales a peculiar smell when warmed or rubbed. When precipitated upon iron, it forms octohedra, but the crystals obtained during the cooling of fused copper are rhomboidal, and have a different place in the thermoelectric series. (SEEBECK.) Copper is frequently thrown down by voltaic action in octohedral crystals; and Wöhler has shown that the small glittering particles in *avanturin glass*, formerly in much request for ornamental articles, and made at Murano, near Venice, are crystals of metallic copper; they form a beautiful microscopic object. (*Ann. der Chem. und Pharm.*, Jan. 1843.) It melts at a cherry-red or dull-white heat; or, according to Daniell, at a temperature intermediate between the fusing-points of silver and gold = 1996° Fahr., and when in fusion has the property of absorbing small quantities of oxygen, which escape again when the metal solidifies, occasioning a spirting and throwing out of portions of the liquid metal. At a very high temperature, copper boils, and, exposed to air, it emits fumes which condense upon cold surfaces into minute globules of protoxide with a metallic nucleus. (DUMAS.) Its specific gravity varies from 8.788 to 8.958; the former being the least density of cast copper, the latter the greatest of rolled or hammered copper. The sp. gr. of some samples of copper containing a little of the protoxide, does not exceed 8.5, and such copper is of inferior ductility. When copper is in a state of extreme division, it burns like tinder, and, under a flame urged by oxygen gas, it takes fire, and burns with a beautiful green light. Exposed for a long time to damp air, copper becomes covered with a thin greenish crust of hydrated oxide and carbonate. If heated and plunged into water, a quantity of reddish scales separate, consisting of an imperfect oxide. The same scales fly off during cooling from a plate of the metal which has been heated red-hot. Copper does not decompose water

at a red-heat. The equivalent of copper is 32. (31.6 TURNER: 31.71 GRAHAM: 32 GMELIN.)

Native copper occurs in a variety of forms; massive, dendritic, granular, and crystallized in cubes, octohedra, &c. It is found in Cornwall, Siberia, Saxony, Hanover, Sweden, and America; chiefly, but not exclusively, in primitive rocks.

COPPER AND OXYGEN. There are two oxides of copper, a *suboxide* or *dioxide*, Cu_2O , and a protoxide, CuO : the latter is the basis of the stable and common salts of copper; the dioxide combines directly with only a few of the acids, and is in most cases resolved by them into metallic copper and protoxide; $\text{Cu}_2\text{O} = \text{Cu} + \text{CuO}$.

SUBOXIDE OF COPPER. DIOXIDE OF COPPER. Cu_2O . This oxide occurs *native*; it may be formed artificially, (1.) By exposing thick copper wire in a muffle to a bright red-heat, so as just not to fuse it, for about half an hour, and then keeping it for some hours at a dull red-heat; it thus forms a dark crystalline coating upon the core of metallic copper. (MARCHAND.) (2.) By heating 5 parts of peroxide with 4 of very finely divided metallic copper; or, according to Turner, by arranging thin copper plates one above the other, with interposed strata of the black oxide, and exposing them to a red-heat carefully protected from the air. (3.) By fusing 5 parts of dichloride of copper with 3 of dry carbonate of soda, and washing and drying the residue. (4.) By fusing a mixture of 100 parts of crystals of sulphate of copper, with 57 of crystals of carbonate of soda; when the water is expelled, the mass is reduced to powder, mixed with 25 parts of copper filings, and exposed to a white-heat for about 20 minutes; the residue is then pulverized, washed, and dried; it is of a red color, the tint being improved by trituration and washing. This, which is Malaguti's process, is the most economical and yields the best product. (*Ann. Ch. et Ph.*, liv. 216.) (5.) By adding to an aqueous solution of equal weights of sulphate of copper and sugar a sufficiency of soda to redissolve the first precipitate, and then boiling the resulting blue liquor: the suboxide falls as a brown, and often crystalline powder, which, when washed and dried, is permanent in the air. (MITSCHERLICH.) (6.) *Hydrated* suboxide of copper is precipitated in the form of a dingy orange-colored or brown powder, when a hot solution of subchloride of copper is decomposed by potassa: if dried in *vacuo* it becomes reddish-brown. (7.) When sulphate of copper and protosulphate of iron are dissolved in water and precipitated by an alkali, dioxide of copper and peroxide of iron are thrown down: the former may be separated by digestion, out of the contact of air, in ammonia, which gives a colorless solution. (LEVOL, *Ann. Ch. et Ph.*, lxxv. 320.) (8.) Moist hydrated oxide of copper is boiled for a few minutes in a solution of sugar of milk, containing a little potassa or soda; the liquor is then diluted, and the precipitate washed: it is orange-yellow. (BÖTTGER.) (9.) When grape sugar is boiled in a solution of tartrate of copper in soda, or carbonate of soda, a yellow hydrated dioxide of copper falls, which on drying assumes a red color, often of considerable brilliancy. (See SUGAR.)

Dioxide of copper is fusible: it passes into protoxide when heated in the air. When intensely heated in close vessels, small octohedral and

cubic crystals are frequently formed in it; the same thing was observed by Chenevix, on exposing peroxide of copper to a violent heat, in an open crucible; a semi-fused mass, resembling native red copper, was obtained. (*Phil. Trans.*, 1801.) The dilute acids mostly resolve this oxide into metallic copper and peroxide; it dissolves in concentrated hydrochloric acid; it also dissolves in ammonia, as will presently be explained; it is not soluble in solutions of potassa or of soda. Its salts are frequently formed by the action of deoxidizing agents on the protosalts. It consists of

						Chenevix.	Berzelius.
Copper	2	64	88·9 88·5 88·97
Oxygen	1	8	11·1 11·5 11·03
<hr/>							
Dioxide of copper....	1		72		100·0	100·0	100·00

Copper vessels, such as tea-urns, &c., and medals, are often superficially coated with this oxide, or *bronzed*; it gives them an agreeable appearance, and prevents tarnish. For this purpose two processes are resorted to: (1.) The copper surface is cleaned, and then brushed over with peroxide of iron (generally colcothar) made into a paste with water, or with a very dilute solution of acetate of copper; heat is then cautiously applied in a proper furnace or muffle, till it is found, on brushing off the oxide, that the surface beneath has acquired its proper hue. “The red oxide of iron is thus reduced to protoxide, 2Cu, and Fe2 O3, giving Cu2O and 2FeO: this last is removed by digestion in a boiling solution of acetate of copper.” (KANE.) (2.) 2 parts of verdigris and 1 of sal-ammoniac are dissolved in vinegar: the solution is boiled in a pipkin, skimmed, and diluted with water till it only tastes slightly of copper and ceases to deposit a white precipitate; it is then poured into another pipkin or copper pan, and rapidly brought to boil, and the medal, previously rendered bright, and *perfectly clean*, is dipped into the boiling solution, which may be most conveniently done by placing it in a small perforated copper-ladle or wire-colander made for the purpose: the surface of the medal becomes at first black or dark-blue, and then (in about 5 minutes) acquires the desired brown tint; it must then be instantly withdrawn, (otherwise it changes color,) and washed in a stream of water so as perfectly to remove all soluble matter from its surface; and lastly, very carefully wiped and dried. The medal is generally perfected by afterwards giving it one gentle pinch between the dies, in the coining-press. When there are many medals, each must be done separately, as they must not be allowed to touch each other, and care should be taken to rest them upon as few points of contact as possible. The bronzing-liquid also must not be suffered to concentrate by evaporation, but must be diluted if necessary, so as to keep it in a proper state, and especially to avoid all appearance of a white precipitation in it. It is better that the process should be too slowly than too rapidly effected. Medals and voltatypes may also be bronzed by covering their surface with plumbago, heating them to dull redness, and then brushing the surface till it acquires the desired tint.

Native Oxide of Copper, or Ruby Copper, is of a red or steel-grey color, soft and brittle, and occurs massive, and crystallized in octohedra, dodecahedra, and cubes. Its specific gravity is 5·6 to 6. There is a beautiful variety in fine *capillary* crystals; and another, which is compac

earthy, and contains more or less peroxide of iron, called *Tile Ore*. Cornwall abounds in fine specimens of this ore.

PROTOXIDE OF COPPER. CuO . (1.) When copper is exposed to heat and air, its surface tarnishes, acquiring a yellow and then a violet color, and at a high temperature black scales form upon it, which are thrown off on plunging it into water, or which fly off as it cools, in consequence of the comparatively rapid contraction of the metal. When these scales are reduced to a fine powder, and stirred in contact of air at a red-heat, they yield the protoxide of copper. (2.) When nitrate of copper is exposed to heat gradually raised to redness, it fuses and is decomposed, and ultimately this oxide remains.

Protoxide of copper is black, or bluish, or brownish-black; its specific gravity is 6.4. Before the blow-pipe, it fuses when intensely heated by the tip of the flame, upon charcoal: by the interior of the flame it readily affords a globule of metal. It is generally stated that when heated alone it loses no oxygen, but, according to Favre, it fuses at a temperature approaching that at which copper melts, and loses 8 *per cent.* of oxygen, and is converted into a suboxide $= \text{Cu}_5\text{O}_3$. (*Comptes Rendus*, April, 1844.) It is easily and rapidly decomposed at a dull red-heat, or even below it, by hydrogen; at the same temperature, also, carbon speedily reduces it, and, if the mixture be in proper proportions and suddenly heated, a kind of deflagration takes place; it is also decomposed when heated in contact with organic substances, converting their hydrogen into water, and their carbon into carbonic acid; hence its use in their analysis; it is very hygrometric, and if weighed whilst hot, augments in weight after cooling, in consequence of the absorption of aërial moisture. It is insoluble in water, but it dissolves in, or combines with, the greater number of the acids, and is the basis of all the common salts of copper. When alkalis are dropped into its solutions, they throw it down as a bulky blue *hydrate*, which, however, is not permanent at a boiling heat, but becomes black and anhydrous. This oxide of copper is not soluble in the liquid fixed alkalis; (soluble to a small extent, and under certain circumstances, according to Proust and Chodnew. *Chem. Gaz.*, Aug., 1843;) but when carbonate of potassa or of soda are fused with it, it expels carbonic acid, and combines to form a blue or green compound. Its combination with ammonia will presently be noticed. It communicates a green, and sometimes a blue tint to vitreous compounds; and Sir H. Davy has shown that it is the basis of certain colors used by the ancients, which had been supposed to contain cobalt. (*Phil. Trans.*, 1815.) It consists of

						Proust.		Berzelius.		Gay Lussac.
Copper	1	32	80	80	80.13 80.28
Oxygen	1	8	20	20	19.87 19.72
<hr/>										
Protoxide of copper	1		40		100		100		100.00	100.00

This oxide is sometimes considered as a *deutoxide*, and the dioxide as a *protoxide*: in this case 64 becomes the equivalent of copper; but the dioxide has such feeble basic powers and is so unstable, that it can scarcely be regarded as the true protoxide, or compound containing single atoms of its components: it may also be observed, (1.) That the general characters

of a suboxide belong to the red oxide; (2.) That the equivalent of copper deduced from its specific heat (p. 62) is about 32; and (3.) that the salts of the black oxide of copper are isomorphous with those of the protoxide of iron; which gives a strong presumption that those oxides possess the same atomic constitution. (TURNER.) (4.) To these arguments it may be added, that the electro-chemical equivalent of copper appears to be 32.

HYDRATED PROTOXIDE OF COPPER, CuO, HO , as thrown down from a solution of sulphate of copper by dilute potassa or soda, is at first of an agreeable blue color, but this soon changes to green, especially if it be dried: it sustains, when dry, a temperature of 212° without decomposition, but a little above that it becomes discolored: when boiled in the liquor from which it has been precipitated, or when a solution of copper is added to a boiling solution of soda or potassa, it becomes anhydrous and nearly black. Alcohol does not decompose it. When this hydrated oxide of copper is used as a pigment, or color for paper-staining, it is rendered more permanent by mixing it with glue or size, and chalk or alumina are also generally added: it, however, soon acquires a green tinge. Dumas gives the following process for preparing a blue color with this hydrate: 6 parts of sulphate of copper and 3 parts of chloride of calcium are dissolved in separate portions of water; the solutions are then mixed, and when the sulphate of lime has subsided the solution of chloride of copper is poured off and mixed with cream of lime, containing $1\frac{1}{2}$ parts of quicklime: the mixture is well agitated, and the greenish precipitate which falls, and which is an oxichloride of copper, being well drained, is ground up with a fourth part of lime and a fourth part of potash of commerce, so as to form a mixture of proper consistency. When this paste is put into bottles, a fourth part of sal-ammoniac and half a part of sulphate of copper are added to improve the color, which, however, cannot be depended on, as it is apt to become green when dry, so that it is generally sold in the form of paste, to avoid the risk of desiccation.

COPPER AND CHLORINE. Gaseous chlorine acts upon finely-divided copper with great energy, and produces *two* chlorides; the one a comparatively fixed fusible substance, which is the *dichloride*: the other a yellow substance, which is a *protochloride*.

DICHLORIDE OF COPPER, Cu_2Cl , was first described by Boyle in 1666, under the name of *Resin of Copper*. It was afterwards examined by Proust, who called it *White Muriate of Copper*. (*Ann. de Chim.*, xxviii. 218.) It may be obtained by exposing copper filings to the action of chlorine not in excess: or by evaporating the solution of dioxide of copper (or of 1 atom of metallic copper and 1 of protoxide) in hydrochloric acid, and heating the residue in a vessel with a very small orifice; or by heating the protochloride in the same way. It is also the residue of the distillation of a mixture of 2 parts of corrosive sublimate and 1 of copper filings. When protochloride of tin is added to any of the soluble salts of copper, or when protochloride of copper and sugar are boiled in water, this dichloride is also formed. It is insoluble in water, but soluble

in hydrochloric acid, from which potassa throws down the hydrated dioxide: when water is added to its hydrochloric solution, it is thrown down in the form of a white granular hydrate: its color varies, being generally dark-brown when fused, but if slowly cooled, it is yellow, translucent, and crystalline; when in fine division it is white: it must be preserved out of contact of air. By nitric acid it is first rendered blue and then green; it is not affected by dilute sulphuric acid: with ammonia it forms a colorless solution extremely susceptible of change by air, and then becoming deep blue. It consists of

					J. Davy.
Copper	2	64	64
Chlorine	1	36	36
<hr/>					
Dichloride of copper	1		100		100

When moistened dichloride of copper is exposed to air, it acquires a green color, and becomes converted into a compound of chloride and oxide of copper, which has been termed *Submuriate of copper*, or *Brunswick green*; the same compound may be formed by adding hydrated oxide of copper to a solution of the chloride; or by exposing to the atmosphere slips of copper partially immersed in hydrochloric acid. This compound consists, according to John Davy, of 4 atoms of protoxide of copper, 1 of hydrochloric acid, and 3 of water.

CHLORIDE OF COPPER. **PROTOCHLORIDE OF COPPER,** CuCl , may be formed by heating copper filings in excess of chlorine, or by dissolving protoxide of copper in hydrochloric acid, and evaporating to dryness by a heat below 400° . Dumas obtains it by decomposing sulphate of copper by chloride of calcium: the sulphate of lime is separated by filtration, the solution is then evaporated to the consistence of syrup and mixed with alcohol, which dissolves the chloride without touching the sulphate.

Protochloride of copper is brown or yellowish when dry and anhydrous, but becomes blue by exposure to air; it is soluble in water and alcohol and very difficultly crystallizable. The prismatic crystals are $\text{CuCl}, 2\text{HO}$. Exposed to a red-heat in a tube with a very small orifice, gaseous chlorine is expelled, and it becomes a dichloride. When it is acted upon by potassa not added in excess, and only so as partially to decompose it, a green oxichloride is thrown down, being, according to Dumas, identical with the native compound. This chloride consists of

						J. Davy.
Copper.....	1	32	47 47
Chlorine	1	36	53 53
<hr/>						
Protochloride of copper	1		68		100	100

OXICHLORIDE OF COPPER, $3\text{CuO}, \text{CuCl}, 4\text{HO}$, is found *native* in Peru and Chili, sometimes in the form of green sand, and sometimes massive and crystallized. The *green sand* was first found in the river Lipas, in the desert of Atacama, separating Peru from Chili; hence mineralogists have termed this variety *Atacamite*. Chloride of copper has also been found upon some of the lavas of Vesuvius. The primitive form of this substance is an octohedron. It is of a deep-green color, and contains, accord-

ing to Dr. Davy's analysis, 73 of oxide of copper, 16·2 of hydrochloric acid, and 10·8 of water ; but, according to Dumas,

Protoxide of copper	3	120	53·5
Protochloride of copper	1	68	30·5
Water	4	36	16·0
<hr/>					
Native oxichloride of copper.....	1		224		100·0

Several other combinations of oxide and chloride of copper with variable proportions of water have been described. Dr. Kane observes that the compound thrown down from the solution of chloride of copper by an alkali (and called Brunswick green?) is $\text{CuCl}, 3\text{CuO}, \text{HO}$, and that there are two other oxichlorides having the formulæ $\text{CuCl}, 2\text{CuO}, 3\text{HO}$, and $\text{CuCl}, 4\text{CuO}, 6\text{HO}$, prepared by the decomposition of the ammoniacal chlorides of copper.

AMMONIO-CHLORIDES OF COPPER. (1.) $3\text{NH}_3, \text{CuCl}$, is the result of the absorption of gaseous ammonia by protochloride of copper: it forms a bulky blue powder which when heated evolves ammonia, then fuses, sal-ammoniac sublimes, and dichloride of copper remains. (FARADAY. II. ROSE.) (2.) $2\text{NH}_3, \text{CuCl}$. When gaseous ammonia is passed through a hot saturated solution of protochloride of copper till the first formed precipitate is redissolved, small dark-blue octohedral crystals are deposited on cooling, which are $2\text{NH}_3, \text{CuCl}, \text{HO}$. (KANE.) (3.) NH_3, CuCl , formed when either of the preceding compounds is heated to 300° . At higher temperatures nitrogen, ammonia, and sal-ammoniac are evolved, and dichloride remains: $6\text{NH}_3, \text{CuCl} = 3[\text{Cu}_2 \text{Cl}] + 3[\text{NH}_3, \text{HCl}] + 2\text{NH}_3 + \text{N}$. (KANE.) (4.) When a concentrated aqueous solution of sal-ammoniac and protochloride of copper in single atomic equivalents is cooled till it crystallizes (or crystallized by evaporation in vacuo?) it gives green octohedral crystals $= \text{NH}_4 \text{Cl}, \text{CuCl}, 2\text{HO}$. (MITSCHERLICH.) The dilute aqueous solution of this salt deposits a green powder, and becomes acid. It is soluble in alcohol without decomposition. (CASS and HENRY, *Journ. de Pharm.*, xxiii.)

POTASSIO-CHLORIDES OF COPPER. (1.) $2\text{KCl}, \text{Cu}_2 \text{Cl}$. This compound of 2 atoms of chloride of potassium with 1 of dichloride of copper is obtained in anhydrous octohedral crystals, by boiling the dichloride in a little water, adding chloride of potassium till the whole dissolves, and cooling in a close vessel. (MITSCHERLICH.) (2.) $\text{KCl}, \text{CuCl}, 2\text{HO}$ is deposited in octohedral crystals by cooling a hot concentrated solution of protochloride of copper and chloride of potassium: they are soluble in water and alcohol.

CHLORATE OF COPPER, CuO, ClO_5 , is a blue-green deliquescent salt, difficultly crystallizable, formed by dissolving oxide of copper in chloric acid. A piece of paper dipped into its solution, burns with a remarkably green flame. (VAUQUELIN.) This salt is formed, according to Chenevix, by passing chlorine through a mixture of oxide of copper and water. Waechter obtained it by mixing equivalents of sulphate of copper and chlorate of baryta, and evaporating the filtered solution over sulphuric acid in vacuo; a dark-green liquid was obtained which required an in-

tense cold for solidification, and gave indistinct octohedrons ($\text{CuO}, \text{ClO}_5, 6\text{HO}$.) very deliquescent and soluble in alcohol, fusing at 149° , and decomposed at a somewhat higher temperature into a basic chlorate, and ultimately into chlorine, oxygen, and oxide of copper.

PERCHLORATE OF COPPER. CuO, ClO_7 , obtained by dissolving oxide of copper in aqueous perchloric acid, yielded blue deliquescent crystals soluble in alcohol. (SERULLAS, *Ann. Ch. et Ph.*, xlv. 306.)

SUBIODIDE OF COPPER. DINIODIDE OF COPPER. Cu_2I . When iodide of potassium is added to a solution of the protosulphates of copper and iron, both in crystals, in the ratio of 1 to $2\frac{1}{4}$, the protoxide of iron takes the oxygen of the oxide of copper, and the iodine the metallic copper, with which it forms a white precipitate of the diniodide; it may be dried in close vessels. (TURNER.) When iodide of potassium is added to a salt of protoxide of copper, iodine is set free, and a brown subiodide falls.

Protiodide of copper has not been obtained, for when iodine and finely-divided copper are heated together, it is the subiodide only which is formed; but with ammonia and with potassium double salts are produced, containing a protiodide, giving $2\text{NH}_4\text{O}, \text{CuI}$, and KI, CuI .

IODATE OF COPPER. CuO, IO_5 . When solution of iodate of potassa is added to solutions of copper, a difficultly soluble *iodate of copper* is thrown down. It dissolves in ammonia, forming a crystallizable double salt. There appear to be other iodates of copper, the composition of which has not been clearly determined. (MILLON. *Ann. Ch. et Ph.*, ix. 424.)

PERIODATE OF COPPER. CuO, IO_7 . Periodate of potassa throws down a green precipitate when added to solution of nitrate of copper.

DIBROMIDE OF COPPER. Cu_2Br . Copper presents the same phenomena with bromine as with chlorine; the dibromide is insoluble in water, but soluble without decomposition in hydrochloric acid: sulphuric acid has no action on it. Heated in a tube it is not decomposed, but in the air it gives off vapors which color flame green, and oxide of copper remains. Ammonia dissolves it and yields a crystallizable ammonio-bromide. It is soluble in hydrobromic acid; the solution is colorless, and gives a precipitate of metallic copper when a solution of protosulphate of iron is added to it. $\text{Cu}_2\text{Br} + 3[\text{FeO}, \text{SO}_3] = 2\text{Cu} + \text{FeBr} + \text{Fe}_2\text{O}_3 + 3\text{SO}_3$.

PROTOBROMIDE OF COPPER, CuBr , is formed by dissolving protoxide of copper in hydrobromic acid; the solution is green, but becomes brown by evaporation and yields acicular crystals extremely deliquescent $= \text{CuBr}, 5\text{HO}$. Evaporated to dryness it acquires a grey metallic lustre like plumbago. (SERULLAS.) There are two ammonio-bromides of copper, namely, $5\text{NH}_3, 2\text{CuBr}$, and $3\text{NH}_3, 2\text{CuBr}$. (RAMMELSBERG. *Poggend.*)

BROMATE OF COPPER, $\text{CuO}, \text{BrO}_5, 5\text{HO}$. Green crystals obtained from a solution of hydrated oxide in bromic acid. Dissolved in ammonia and

precipitated by alcohol, a blue crystalline precipitate falls $= 2\text{NH}_3, \text{CuO}, \text{BrO}_5$. (RAMMELSBERG.)

FLUORIDES OF COPPER. When hydrated dioxide of copper is added to hydrofluoric acid, and evaporated out of the contact of air, a fusible compound of a black color while hot, but becoming red as it cools, is obtained, which is a *difluoride of copper*. It forms a dark solution in hydrofluoric acid, and is precipitated white by water, but becomes red when collected upon a filter. It is permanent when dry, but when moist it becomes by exposure to air first a yellow mixture of protofluoride and hydrated dioxide, $2\text{Cu}_2\text{F} + \text{O} = 2\text{CuF} + \text{Cu}_2\text{O}$, and this passes into a green oxifluoride of copper, $2\text{CuF} + \text{Cu}_2\text{O} + \text{O} = 2[\text{CuF}, \text{CuO}]$.

When hydrated oxide or carbonate of copper are dissolved in hydrofluoric acid, small blue crystals may be obtained on evaporation $= \text{CuF}, 2\text{HO}$: they are difficultly soluble in cold water, and are resolved by boiling into an acid salt which remains in solution and an insoluble basic compound $= \text{CuF}, \text{CuO}, \text{HO}$; or $2\text{CuO}, \text{HF}$. (BERZELIUS, as quoted by Gmelin.)

COPPER AND HYDROGEN. HYDRURET OF COPPER, Cu_2H . A mixed solution of sulphate of copper and hypophosphorous acid heated to about 160° , gives a brown precipitate composed of 98.78 copper, 1.22 hydrogen. When heated it gives off hydrogen: it burns in chlorine; and with hydrochloric acid it evolves a double volume of hydrogen, forming dichloride of copper. (WURTZ. *Comptes Rendus*, xviii. 702.)

COPPER AND NITROGEN. NITRURET OF COPPER. Cu_6N . It was long ago observed by Thenard, that ammonia passed over red-hot copper wire was decomposed, and that the metal became at the same time peculiarly brittle. Savart afterwards remarked that the copper sustained a sensible increase of weight and diminution of sp. gr. (*Ann. Ch. et Ph.*, xxxv. 326.) Despretz found the sp. gr. of the copper reduced to 5.5, its texture crystalline, and its surface iridescent. (*Ann. Ch. et Ph.*, xlii. 122.) Pfaff observed, that on decomposing ammonia by passing it over ignited copper, the resulting nitrogen and hydrogen were not to each other as 25 to 75, but as 14 to 86, and suspected, therefore, that a part of the nitrogen must have been retained by the copper, (*Poggend*, xlii., 184;) but Schrötter could not detect this diminution. (*Ann. der Pharm.*, xxxvii. 131.) Grove, by electrizing certain metals in solution of sal-ammoniac, found the negative metal changed in properties, and ascribed this to combined nitrogen; copper thus treated became brown, its sp. gr. was reduced to 5.9, and 10 grains of it yielded 0.214 cub. in. of nitrogen gas. (*Phil. Mag.* xix.)

When dry ammonia is passed over pure oxide of copper heated in an oil-bath to 482° for eight hours, or till water is no longer evolved, nitrogen is set free, and a green powder is found in the tube; [at higher temperatures the only result is metallic copper.] The green powder was removed, rubbed down in a mortar, and again submitted to the action of the gaseous ammonia, and after having been digested in a mixture of caustic and carbonated ammonia to separate suboxide, it was of a grey color, and gave 7 per cent. of nitrogen. (SCHRÖTTER.) Heated in the air,

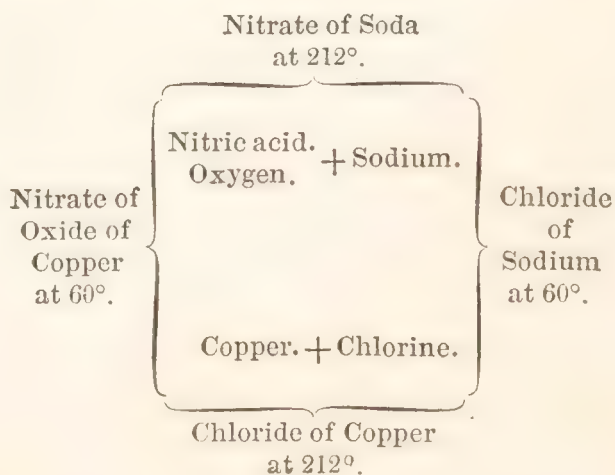
it ignites at 570° , and gives off nitrogen. In oxygen, it burns at a lower temperature: with chlorine it gives chloride of copper and nitrogen. In its production, it appears that $6\text{CuO} + 2\text{NH}_3$ give Cu_6N , $+ 6\text{H}_2\text{O}$, $+ \text{N}$, (GMELIN,) its composition being

						Schrötter.
Copper	6	...	192	...	93.2	92.76
Nitrogen	1	...	14	...	6.8	7.24
<hr/>						<hr/>
Nitruet of copper	1		206		100.0	100.00

NITRATE OF COPPER. $\text{CuO}, \text{NO}_5, 3\text{H}_2\text{O}$. Nitric acid diluted with 3 parts of water rapidly oxidizes copper, evolving nitric oxide, and ultimately forming a bright-blue solution, which affords deliquescent prismatic crystals on evaporation, of a fine blue color, caustic, and very soluble in water and in alcohol. They liquify at a temperature below 212° ; at a higher temperature they lose water and acid, becoming a *subnitrate*, and are entirely decomposed at a red-heat, leaving protoxide of copper. They consist of

Oxide of copper.....	1	...	40	...	33.06
Nitric acid	1	...	54	...	44.63
Water	3	...	27	...	22.31
<hr/>					
Prismatic nitrate of copper	1		121		100.00

At low temperatures this salt sometimes crystallizes in rhomboidal plates, which contain 6 atoms of water, but these effloresce into the terhydrate in vacuo over oil of vitriol, and all attempts at its further dehydration lead to decomposition, so that anhydrous nitrate of copper cannot be obtained. Potassa forms, in the solution of this nitrate, a bulky blue precipitate of *hydrated oxide of copper*, which, as already observed, when boiled in potassa or soda, becomes black from the loss of its combined water. When nitrate of copper is coarsely powdered, sprinkled with a little water, and quickly rolled up in a sheet of tin-foil, there is great heat produced, nitrous gas is rapidly evolved, and the metal often takes fire. (HIGGINS, *Phil. Trans.*, LXIII.) If ammonia be added to solution of nitrate of copper, it occasions a precipitate of the hydrated oxide; but if it be added in excess, the precipitate is redissolved, and an *ammonio-nitrate* is produced. When solutions of nitrate of copper and chloride of sodium are mixed at common temperatures, the mixture remains blue, and no decomposition ensues; but on raising its temperature to 212° , it becomes of a vivid green, indicating the formation of chloride of copper; on again cooling, the blue color returns, and this interchange of elements may be repeated any number of times. On evaporating the mixed solutions to a small bulk, chloride of copper is permanently formed, and rhomboidal crystals of nitrate of soda are deposited. In the annexed diagram the vertical brackets point to the state of the salts at 60° , and the horizontal to that at 212° .



SUBNITRATE OF COPPER. $3\text{CuO}, \text{NO}_5, \text{HO}$. When the neutral nitrate of copper is exposed to a temperature between 500° and 600° , or when alkali is added to a solution of that salt, in quantity insufficient for complete decomposition, this subnitrate is obtained in the form of an insoluble green powder (*trisnitrate*.) "When oxide of copper is drenched with the most concentrated nitric acid, it is this subsalt, singular as it may appear, which is formed, even when the acid is in great excess: the reason seems to be, that the nitrate of water, being deficient in constitutional water, assumes 3 atoms of oxide of copper in its place." (GRAHAM.) [Graham's views in reference to the basic and constitutional water of nitric acid (sp. gr. 1.42) and of the "magnesian nitrates," including those of oxide of copper, will be found in his *Elements of Chemistry*, p. 296.]

AMMONIA AND OXIDE OF COPPER. When copper filings are digested in aqueous ammonia exposed to air, the solution soon becomes blue: if air be then excluded, it gradually loses color, but again acquires a blue color on the contact of air: in the blue liquor the copper exists as *protoxide*; in the colorless liquor as *dioxide*. (BERGMANN.) If a tall glass jar be filled with liquid ammonia and a few drops of solution of dioxide of copper (protochloride) added, the surface becomes blue, but it remains colorless below.

The solution of the protoxide of copper in ammonia is obtained by exposing copper filings in solution of ammonia to air, or by dissolving the hydrated oxide in ammonia: it is of a splendid deep-blue color; phosphorus and zinc decompose it, and copper is precipitated; sulphurous acid throws down the greater part of the copper in the state of suboxide; potassa separates the hydrated oxide, which also falls when the deep-blue liquor is very largely diluted with water: at a boiling heat the black oxide falls.

According to Berzelius, when carbonic and all other acids are entirely excluded, aqueous ammonia scarcely dissolves dry oxide of copper, but the addition of a minute portion of any ammoniacal salt renders it active. No definite, or crystalline compound of ammonia and oxide of copper can be obtained. Levöl proposes to apply the reduction by copper of the ammoniacal protoxide to the quantitative determination of metal in cupreous salts. (*Ann. Ch. et Ph.*, 3rd Ser., iv. 381.)

AMMONIO-NITRATE OF COPPER. When a hot and strong solution of nitrate of copper is decomposed by excess of ammonia, and allowed to cool, this salt crystallizes in anhydrous rhombic octohedrons of a purple color $= 2\text{NH}_3, \text{CuO}, \text{NO}_5$; Kane represents this salt by the formula $\text{Cu}, \text{NH}_2, + \text{NH}_4\text{O}, \text{NO}_5$, that is, as a compound of amidide of copper with nitrate of oxide of ammonium.

COPPER AND SULPHUR. DISULPHURET OF COPPER, Cu_2S , may be formed artificially, by heating a mixture of copper filings and sulphur: as soon as the latter melts, a violent action ensues, the copper becomes red-hot, and a black brittle compound is formed, sp. gr. 5.97. It may also be produced by fusing sulphur with oxide of copper. According to Wintelblech, when 64 parts, or 2 atoms of finely-divided copper, obtained

by the reduction of carbonate of copper by hydrogen, and 16 parts, or 1 atom of dry and finely-divided sulphur, (precipitated sulphur dried over oil of vitriol,) are carefully rubbed together, they combine with ignition to form this disulphuret: if the atomic weights are not very accurately adhered to, the experiment fails. (*Ann. der Pharm.*, xxi. 34.)

Disulphuret of copper is difficultly soluble in boiling hydrochloric acid, yielding a solution of dichloride of copper, and evolving sulphuretted hydrogen. Warm nitric acid dissolves it with the separation of sulphur: cold nitric acid abstracts half the copper, and leaves protosulphuret. It is soluble in hydrochloric acid, with the evolution of sulphuretted hydrogen; and in nitric acid, with the separation of sulphur. It consists of

						Berzelius.		Vauquelin.		Klaproth. <i>Native.</i>	
Copper.....	2	64	80	79·73	78·69	76·5
Sulphur	1	16	20	20·27	21·31	22·
<hr/>											
Disulphuret of copper	1		80		100		100·00		100·00		98·5

Native Disulphuret of Copper. Vitreous Copper. This ore of copper is chiefly found in primitive countries. In England, it occurs in great beauty, crystallized and massive, in Cornwall, and in Yorkshire. Its color is grey; its lustre shining and metallic; and it yields easily to the knife. Its sp. gr. 5·69 to 5·73. Its primitive form is a six-sided prism, which passes into the dodecahedron with triangular faces, and its various modifications. A variety of *black sulphuret of copper*, containing iron and arsenic, has been described by W. and R. Phillips, under the name of *Tennantite*; its most ordinary form is the rhomboidal dodecahedron, either perfect or variously modified. (*Quar. Jour. of Science and Arts*, vii. 95.)

PROTOSULPHURET OF COPPER. CuS . This compound cannot be formed by fusion, but it is thrown down when sulphuretted hydrogen is passed through a solution of protoxide of copper: the precipitate is at first brown, but becomes black, and when dried assumes a greenish hue. In this state it reddens moistened litmus paper, and when heated gives off a little water and sulphurous acid, and sulphur, and the disulphuret remains. It may also be obtained by digesting finely-powdered disulphuret in cold nitric acid till the action ceases, and washing the residue: it remains as a greenish-black powder. (FARADAY.) It sometimes occurs native, associated with disulphuret: it has also been found in the fumaroles of Vesuvius: it is a soft black or bluish amorphous substance. (Indigo-Copper.) (COVELLI, *Ann. Ch. et Ph.*, xxxv. 105.) It consists of

Copper	1	32	66·67
Sulphur	1	16	33·33
<hr/>					
Protosulphuret of copper	1		48		100·00

FERROSULPHURETS OF COPPER. *Copper Pyrites, or Yellow Copper Ore*, is the most important and generally occurring ore, from which the largest proportion of the copper of commerce is derived; it occurs in a variety of forms, its primitive crystal being the regular tetrahedron. The British mines are very productive of this ore. A beautiful iridescent variety occurs in the Ecton mine in Staffordshire. The composition of

the different varieties of copper pyrites, appears in all cases to be sulphur, copper, and iron, but their atomic constitution is not very evident. The *variegated copper* Phillips regards as a compound of 1 atom of sulphuret of iron with 2 of sulphuret of copper. (*Ann. of Phil.*, iii. 87.) *Yellow copper ore* is also a double sulphuret of iron and copper: and, omitting the small portion of lead and arsenic with which it is usually contaminated, it may be considered as a compound of 2 atoms of sulphuret of iron and 1 of sulphuret of copper. (PHILLIPS, *Ann. of Phil.*, iii. 301.)

REDUCTION OF THE SULPHURETS OF COPPER. The following is an outline of the processes by which these ores of copper are reduced, as carried on upon a very large scale near Swansea, where the chief part of the Cornish ores are brought to the state of metal. The ore, having been picked and broken, is heated in a reverberatory furnace, by which arsenic and sulphur are driven off. It is then transferred to a smaller reverberatory, where it is fused, a large portion of the sulphuret of iron having been converted into oxide, which, by the addition of silicious sand, forms a vitreous slag: this is occasionally removed, and cast into oblong masses, which are used as a substitute for bricks. When the iron is thus separated, the sulphur begins to burn out of the sulphuret of copper, and the copper becoming oxidized, is reduced by the carbonaceous matter. The impure metal collected at the bottom of the furnace is then granulated by letting it run into water: it is afterwards remelted and granulated two or three times successively, in order further to separate impurities, which are chiefly sulphur, iron, and arsenic, and ultimately cast into oblong pieces called *pigs*, which are broken up, roasted, and melted with a portion of charcoal in the refining furnace. Malleability is here conferred upon the copper, and its texture improved, by stirring the metal with a pole of green wood, generally birch, which causes great ebullition and agitation; assays are occasionally taken out, and the metal, originally crystalline and granular when cold, now becomes fine and close, so as to assume a silky polish when the assays are half cut through and broken. The metal is now cast into cakes about 12 inches wide by 18 in length. The whole process of refining the copper, and toughening it by *poling*, requires much care and attention; and if it be over-poled, the metal is even rendered more brittle than in its original state. The effect of *poling* has not been satisfactorily explained: it may consist in the separation of a small portion of oxide of copper, and the effect of over-poling may possibly depend upon the combination of the copper with a portion of carbon. Copper for brass-making is granulated by pouring the metal through a perforated ladle into water; when this is warm the copper assumes a rounded form, and is called *bean-shot*; but if a constant supply of cold water is kept up it becomes ragged, and is called *feathered-shot*. Another form into which copper is cast, chiefly for exports to the East Indies, is in pieces of the length of six inches, and weighing about 8 ounces each: the copper is dropped from the moulds, immediately on its becoming solid, into a cistern of cold water, and thus, by a slight oxidation of the metal, the sticks acquire a rich red color on the surface. This is called *Japan copper*. A large quantity of copper is rolled into sheets and sheathings, both for exports and home consumption. (For an

excellent account of the reduction of copper, as carried on in this country, see VIVIAN, *Ann. of Phil.*, N.S., v. 113.)

HYPOSULPHITE OF SUBOXIDE OF COPPER, $\text{Cu}_2\text{O}, \text{S}_2\text{O}_2$, was formed by Herschel by mixing hyposulphite of potassa with sulphate of copper. It is colorless; of an intensely sweet taste; and, provided air be excluded, it is not turned blue by ammonia. (*Edin. Phil. Journ.*, i. 24.) Rammelsberg has described two *double hyposulphites of potassa and suboxide of copper*, having the formulæ $\text{KO}, \text{Cu}_2\text{O}, 2\text{S}_2\text{O}_2, 2\text{HO}$; and $3\text{KO}, \text{Cu}_2\text{O}, 4\text{S}_2\text{O}_2, 3\text{HO}$.

SULPHITE OF SUBOXIDE OF COPPER, $\text{Cu}_2\text{O}, \text{SO}_2$, may be obtained by passing sulphurous acid into water through which oxide of copper is diffused; small red crystals are formed, $= \text{Cu}_2\text{O}, \text{SO}_2, 2\text{HO}$. In their production, $3\text{CuO} + 2\text{SO}_2 = \text{CuO}, \text{SO}_3 + \text{Cu}_2\text{O}, \text{SO}_2$; so that sulphate of the protoxide is at the same time formed. When sulphite of potassa is added to nitrate of copper a precipitate falls, which assumes the form of red and yellow crystals; the former are the sulphite of copper; the latter *sulphite of potassa and suboxide of copper*. (CHEVREUL, *Ann. de Chim.*, LXXXiii. 181 and 214.) When bisulphite of potassa, prepared by supersaturating a solution of potassa with sulphurous acid, is mixed with solution of sulphate of copper, the mixture filtered, and then heated, sulphurous acid is evolved, and small dark-red crystals of this double sulphite of potassa and suboxide of copper are deposited. (BOURSON.)

SULPHITE OF COPPER. CuO, SO_2 . Carbonate of copper dissolves with effervescence in a cold aqueous solution of sulphurous acid, forming a green liquor, which gradually becomes blue, and deposits red crystals, which, however, are the salt of the suboxide: this change is accelerated by the direct solar rays, and is very rapid when aided by a gentle heat. (BERTHIER.)

HYPOSULPHATE OF COPPER, $\text{CuO}, \text{S}_2\text{O}_5, 4\text{HO}$, is formed by adding a solution of sulphate of copper to one of hyposulphate of baryta; it crystallizes in small prisms, very soluble in water, but insoluble in alcohol, and slightly efflorescent. When a little ammonia is added to its solution a green powder falls, which is a *subhyposulphate*, composed of 4 atoms of oxide, 1 of acid, and 4 of water. The crystallized neutral hyposulphate contains

						Heeren.
Oxide of copper	1	40	27.03 26.43
Hypsulphuric acid	1	72	48.65 48.10
Water	4	36	24.32 25.47
<hr/>						
Crystallized hyposulphate of copper	1		148		100.00	100.00

SULPHATE OF COPPER. ROMAN VITRIOL. BLUE VITRIOL. CuO, SO_3 . This salt is formed, (1.) By dissolving recently precipitated oxide of copper in diluted sulphuric acid, or by exposing copper to the joint action of moderately dilute sulphuric acid and air. (2.) By boiling copper in sulphuric acid, (either concentrated or diluted with half its bulk of water,) a process which furnishes abundance of sulphurous acid, but which is not

generally had recourse to, to produce sulphate of copper. $\text{Cu} + 2\text{SO}_3 = \text{CuO}, \text{SO}_3 + \text{SO}_2$. (3.) Copper is boiled in sulphuric acid, diluted with 3 or 4 parts of water, and nitric acid gradually added. $3\text{Cu} + 3\text{SO}_3 + \text{NO}_5 = 3 [\text{CuO}, \text{SO}_3] + \text{NO}_2$. (4.) It is made upon a large scale, by exposing roasted sulphuret of copper to air and moisture: thus obtained, it is impure, generally containing iron, and often zinc: it is the common *blue vitriol* of commerce. (5.) It is obtained in large quantities, and very pure, in certain processes afterwards to be described for refining gold and silver. (6.) It is occasionally prepared by dissolving in sulphuric acid an oxichloride of copper, made for the purpose by exposing sheet copper to the joint action of air and hydrochloric acid.

Sulphate of copper forms rhomboidal crystals, (containing 5 atoms of water, $\text{CuO}, \text{SO}_3, 5\text{HO}$,) sp. gr. 2.27, which are sometimes very large and of a beautiful sapphire-blue color, doubly refractive, and liable to slight efflorescence in a moderately dry atmosphere: they are soluble in 4 parts of cold and 2 of boiling water. (3 of cold and 0.5 of boiling water. GMELIN.) It has a peculiarly nauseous metallic taste. When heated to 212° it loses 4 atoms of its water of crystallization, and crumbles down into a pale blue powder; hence, Graham represents it as $\text{CuO}, \text{SO}_3, \text{HO}, + 4\text{HO}$; heated to 400° the whole of its water is expelled, and it becomes white; in this state it slowly re-absorbs water from the air, and regains its blue color; or if sprinkled with water much heat is evolved, and the salt crumbles down into a blue hydrate; by a continued high red or white heat, sulphuric acid, (anhydrous,) and some sulphurous acid and oxygen, are evolved, and oxide of copper remains. Mixed with excess of charcoal and heated to dull redness it is reduced with the evolution of equal volumes of carbonic acid and sulphurous acid. $\text{CuO}, \text{SO}_3, + \text{C} = \text{Cu}, + \text{CO}_2 + \text{SO}_2$. The crystallized salt dissolves in hydrochloric acid, forming a green liquid, which yields crystals of hydrated chloride of copper, and free sulphuric acid. The anhydrous salt rapidly absorbs hydrochloric gas, forming a brown compound, which water resolves into hydrated chloride and free sulphuric acid. The powdered crystallized salt also rapidly absorbs the acid gas, forming a deliquescent green mass, or brown, if much heat is evolved during the action. (KANE.)

This salt is the *Vitriol*, or *Salt of Venus*, of the alchemists. It is much used as a source of several blue and green colors. It is employed by dyers and calico-printers, and is an ingredient in some kinds of writing ink. It has been used to prevent smut in corn, by steeping the grain in a dilute solution of the salt; (*Quart. Journ.*, xvi. 156); and minute quantities of it are occasionally added to bread, (in Paris especially,) to improve its color and texture. (*Archives Gén. de Médecine*, xxi. 145.) In medicine it is resorted to as a powerful emetic; and, in very minute doses, as a tonic. It is also a valuable external application as an astringent, or when undiluted, as a styptic and caustic. It may be employed to prevent *dry rot* by steeping timber or planks in its solution; and it is a powerful preservative of animal substances, which, when imbued with it, and dried, remain unaltered. The waters of copper-mines often hold it in solution, and, when decomposed by immersing in them pieces of iron, yield precipitated metallic copper (*copper of cementation*). The precipitation of metallic copper during the electro-chemical decomposition of an aqueous solution of this salt, and its application in the beautiful

process for obtaining copies of medals and other works of art, has already been alluded to (p. 220).

The elements of sulphate of copper in its anhydrous state are

						Berzelius.
Oxide of copper	1	40	50	50·9
Sulphuric acid	1	40	50	49·1
<hr/>						
Anhydrous sulphate of copper	1		80		100	100·0

The common rhomboidal crystals contain

						Proust.	Berzelius.
Oxide of copper	1	40	32	32	32·13
Sulphuric acid	1	40	32	33	31·57
Water.....	5	45	36	35	36·30
<hr/>							
Crystals of sulphate of copper	1		125		100	100	100·00

When a solution of sulphate of copper is made to crystallize in a warm place, prismatic crystals of a green color are sometimes obtained, which only contain 1 atom of water of crystallization. (THOMSON.) When the common crystals are dried at 100° in vacuo, they leave this monohydrate. When exposed over oil of vitriol, between 65° and 70° , for 7 days, they pass into bihydrate. (GRAHAM.)

DISULPHATE OF COPPER. $2\text{CuO}, \text{SO}_3$. When a solution of sulphate of copper is boiled for a long time with a quantity of oxide of copper equal to that contained in the salt, the solution at last becomes colorless, and a green powder is deposited, containing all the oxide of copper, and all the sulphuric acid: it is therefore a disulphate. (THOMSON.) Denham Smith could not succeed in obtaining this disulphate.

TRISULPHATE OF COPPER. When a solution of sulphate of copper is precipitated by a small addition of potassa, a green, tasteless, insoluble powder falls, being, according to Berzelius, $3\text{CuO}, \text{SO}_3, 3\text{HO}$. D. Smith (*Mem. Chem. Soc.*, i. 223,) could not obtain this salt with 3 atoms of water. By boiling an equivalent of oxide of copper and 2 equivalents of sulphate of copper, Berthollet's subsulphate is formed, of a bright-green color, with a shade of blue, composed of

						D. Smith.
Oxide of copper.....	3	120	67·5	68·60
Sulphuric acid	1	40	22·5	23·30
Water	2	18	10·0	8·10
<hr/>						
Trisulphate of copper	1		178		100 0	100·00

TETRASULPHATE OF COPPER. $4\text{CuO}, \text{SO}_3, 3\text{HO}$. When solutions of sulphate of potassa and sulphate of copper are boiled together, a green powder falls, which, if boiled in repeated portions of water, leaves an insoluble residue, composed, according to the analysis of Brunner, (*Poggend. Ann.*, xv.) of 4 atoms of oxide of copper, 1 of sulphuric acid, and 3 of water. The bluish-green precipitate which falls when ammonia or potassa are added in moderate quantity to sulphate of copper, contains, according to Kane and Graham, 4 atoms of oxide of copper, 1 of sulphuric acid, and 4 of water; and D. Smith mentions a subsulphate with 5 atoms of water.

PENTABASIC SULPHATES OF COPPER. Two salts having respectively the formula $5\text{CuO}, \text{SO}_3, 4\text{HO}$, and $5\text{CuO}, \text{SO}_3, 6\text{HO}$, are also mentioned by D. Smith. In reference to the function of the water contained in these salts, Smith combats the opinions of Graham and Kane, and regards them as compounds of anhydrous sulphate of copper with two or more equivalents of hydrated oxide, as indicated in the following tabular arrangement :

Anhydrous neutral sulphate.....	SO_3, CuO	
Green neutral sulphate.....	Do.	+ HO
Blue neutral sulphate	Do.	+ 5HO
Trisulphate	Do.	+ $2\text{CuO}, 2\text{HO}$
1 Tetrasulphate	Do.	+ $3\text{CuO}, 3\text{HO}$
2 Tetrasulphate	Do.	+ $3\text{CuO}, 3\text{HO}, + \text{HO}$
3 Tetrasulphate.....	Do.	+ $3\text{CuO}, 3\text{HO} + 2\text{HO}$
1 Pentasulphate	Do.	+ $4\text{CuO}, 4\text{HO}$
2 Pentasulphate	Do.	+ $4\text{CuO}, 4\text{HO} + 2\text{HO}$

OCTOBASIC SULPHATE OF COPPER. By adding potassa to a solution of sulphate of copper so as to throw down all the oxide without producing alkaline reaction, Kane obtained an apple-green powder $= 8\text{CuO}, \text{SO}_3, 12\text{HO}$: at 300° it loses 6HO . (GRAHAM, *Elem. of Chem.*, 584; KANE, *Trans. Royal Irish Acad.*, xix.; J. DENHAM SMITH, *Proc. Chem. Soc.*, 1843.)

SULPHATES OF AMMONIA AND COPPER. (1.) *Ammonio-sulphate of Copper*. Anhydrous sulphate of copper rapidly absorbs gaseous ammonia, heats, and forms a bulky blue powder soluble in water, $= 5\text{NH}_3, + 2 [\text{CuO}, \text{SO}_3]$. (H. ROSE.)

(2.) *Cuprosulphate of ammonia*. $\text{NH}_3, \text{CuO} + \text{NH}_4\text{O}, \text{SO}_3$. When a concentrated solution of sulphate of copper is supersaturated by ammonia so as to redissolve the precipitate at first formed, and crystallized by evaporation or by exposure to a low temperature, dark-blue transparent crystals are obtained, soluble in 1.5 of cold water, insoluble in alcohol, and containing 2 atoms of ammonia, 1 of oxide of copper, and 1 of sulphuric acid: they are the *cuprum ammoniacale* of pharmacy, which is generally made by triturating a mixture of crystallized sulphate of copper and carbonate of ammonia, which liquifies in consequence of the separation of the water of crystallization of the salt, and effervesces from the evolution of carbonic acid. The crystals, when exposed to air, lose ammonia, becoming at first opaque and pale blue, and then crumble into a green powder, which, according to Kühn, is a mixture of sulphate of ammonia and basic sulphate of copper. By a heat not exceeding 300° they slowly lose an atom of ammonia and an atom of water, passing into an apple-green powder $= \text{NH}_3, \text{CuO}, \text{SO}_3$, which heated up to 400° parts with a further proportion of ammonia, becoming $\text{NH}_3, 2\text{CuO}, 2\text{SO}_3$, and by gradually heating this to 500° , the residue of ammonia is expelled, and CuO, SO_3 remains. When the aqueous solution of this salt is largely diluted, it deposits basic sulphate of copper. (KANE.)

Sulphate of Ammonia and Copper. $\text{NH}_4\text{O}, \text{SO}_3 + \text{CuO}, \text{SO}_3 + 6\text{HO}$. This salt crystallizes out of the mixed solution of sulphate of ammonia with sulphate of copper: it is soluble in 1.5 of boiling water, and on cooling the greater part of the salt crystallizes: it effloresces in dry air.

SULPHATE OF POTASSA AND COPPER. $\text{KO}, \text{SO}_3 + \text{CuO}, \text{SO}_3 + 6\text{HO}$. This double salt is formed by digesting hydrated oxide of copper in bisulphate of potassa. It crystallizes in rhomboids of a pale blue color, and consists of 1 atom of sulphate of potassa, 1 of sulphate of copper, and 6 of water.

PHOSPHURET OF COPPER, is formed, (1.), by dropping pieces of phosphorus on red-hot copper-wire: it is more fusible than copper: its specific gravity is 7.12. Pelletier found it composed of 100 copper + 20 phosphorus. (2.) When heated dichloride (or disulphuret) of copper is subjected to the action of phosphuretted hydrogen, a black phosphuret is obtained $= \text{Cu}_6\text{P}$: it is insoluble in hydrochloric but soluble in nitric acid. In its formation, $3[\text{Cu}_2\text{Cl}] + \text{PH}_3 = 3\text{HCl}, \text{Cu}_6\text{P}$. (3.) When phosphuretted hydrogen is passed over heated protochloride or protosulphuret of copper, a black phosphuret is formed $= \text{Cu}_3\text{P}$ (containing about 25 *per cent.* of phosphorus). The same compound in a finely-divided state, and therefore easily oxidable, is thrown down when phosphuretted hydrogen is passed for a long time (2 hours) through a solution of a protosalt of copper. $3\text{CuO} + \text{PH}_3 = \text{Cu}_3\text{P} + 3\text{HO}$. (4.) By passing phosphuretted hydrogen at a high red-heat over diphosphate of copper a grey crystalline phosphuret is formed, containing about 34 *per cent.* of phosphorus and therefore a *diphosphuret* $= \text{Cu}_2\text{P}$. (H. ROSE, *Poggend.*)

HYPOSPHOSPHITE OF COPPER. $\text{CuO}, \text{PO}, 2\text{HO}$. Dilute hypophosphorous acid dissolves hydrated protoxide of copper, forming a permanent blue solution, but when concentrated, even in vacuo, the oxide is reduced. (H. ROSE.) By evaporating in vacuo, Wurtz obtained this salt in small blue crystals, which, heated to 150° , suddenly became phosphuret of copper: it is best formed by the decomposition of sulphate of copper by hypophosphite of baryta.

PHOSPHITE OF COPPER. CuO, PO_3 . Rose obtained this salt in the form of a blue precipitate by decomposing a solution of protochloride of copper by phosphite of ammonia: it admits of being washed and dried at a moderate heat, without decomposition, but when its solution in aqueous phosphorous acid is boiled, part of the copper is thrown down in a metallic state. According to Wurtz this phosphite is best obtained by adding phosphorous acid to a solution of acetate of copper, when a granular precipitate soon falls, the composition of which is expressed by the formula $2\text{CuO}, \text{PHO}_4 + 4\text{HO}$. (*Ann. Ch. et Ph.*, Fevr., 1846.)

PHOSPHATES OF COPPER. 1. *Tribasic*, thrown down by adding bibasic alkaline phosphates in excess to solutions of protosalts of copper (the liquor becoming acid) in the form of a green powder, which loses water and becomes brown when heated. (MITSCHERLICH.) 2. *Bibasic*, thrown down by bibasic phosphate of soda added (not in excess) to salts of copper. (H. ROSE.) *Trombolite*, a native phosphate of copper, is $= 2\text{CuO}, \text{PO}_5, 4\text{HO}$. (PLATTNER.) 3. *Quinquibasic*, also found native, (*Phosphorochalcite*, *Pseudomalachite*) is, according to the analysis of Lunn (*Ann. Phil.*, iii. 182), $5\text{CuO}, \text{PO}_5, 5\text{HO}$. Two other native hydrated subphosphates have been described, namely, a *sexbasic* by Kühn $= 6\text{CuO}, \text{PO}_5, 3\text{HO}$; and a *quaterbasic* by Berthier (*Liebitheinite*) $= 4\text{CuO}, \text{PO}_5, 2\text{HO}$.

SELENIURETS OF COPPER. A *diseleniuret* = Cu_2Se , is formed by heating copper filings with selenium: they act with intense ignition, and a black brittle compound results, containing 40 *per cent.* of selenium: it occurs native. By the action of seleniuretted hydrogen on solution of sulphate of copper, a seleniuret is obtained = CuSe . (BERZELIUS.)

SELENITE OF COPPER. When a hot solution of sulphate of copper is mixed with biselenite of ammonia, a precipitate falls, at first yellow, but which afterwards becomes greenish-blue and crystalline = CuO, SeO_2 . When sulphate of copper is decomposed by selenite of ammonia, with excess of ammonia, a green *diselenite* = $2\text{CuO}, \text{SeO}_2$, is precipitated. (BERZELIUS.)

SELENIATE OF COPPER, CuO, SeO_3 , forms hydrated crystals isomorphous with those of sulphate of copper. (MITSCHERLICH.)

CARBURET OF COPPER. The pale yellowish-red and fibrous, or *overpoled*, copper, (see p. 832,) appears to contain combined carbon. (VIVIAN, *Ann. of Phil.*, v. 121.)

CARBONATES OF COPPER. When hot solutions of copper are precipitated by the carbonated fixed alkalis, carbonic acid is evolved, and a bulky *hydrated dicarbonate of copper*, of a green color, falls, = $2\text{CuO}, \text{CO}_2, \text{HO}$. Its tint is improved by repeated washing with boiling water. It is prepared as a pigment under the name of *mineral green*, or *green verditer*, and *subcarbonate of copper*. It consists of

	Native.						Artificial.		
	Phillips.	Klaproth.	Vauquelin.	Berzelius.	Proust.				
Oxide of copper....	2	80	72.07	72.2	70.5	70.00	71.70	69.5	
Carbonic acid.....	1	22	19.82	18.5	18.0	21.25	19.73	25.0	
Water	1	9	8.11	9.3	11.5	8.75	8.57	5.5	
Hydrated dicar- bonate of copper}	1	111	100.00	100.0	100.0	100.00	100.00	100.0	

When it is long boiled in water, or when carefully heated, it becomes of a deep-brown color, and *anhydrous*, according to Colin and Tallefert (*Ann. Ch. et Ph.*, xii. 62); but according to Gay Lussac, the whole of the carbonic acid is in this case evolved. (*Ann. Ch. et Ph.*, xxxvii. 335.) There is a *native anhydrous dicarbonate*, consisting, according to Thomson, of

	Thomson.				
Oxide of copper	2	80	78.43	78.42	
Carbonic acid	1	22	21.57	21.58	
Anhydrous dicarbonate of copper	1	102	100.00	100.00	

When a cold dilute solution of sulphate of copper is decomposed by carbonate of potassa, a blue precipitate falls, which, by careful management during drying, retains its blue color, and is known in commerce under the name of *blue verditer*. It generally contains a little lime. (PHILLIPS, *Quart. Jour.*, iv. 277.) It differs from the green carbonate, according to Colin and Tallefert, only in containing more water; it appears, however, from the following analysis, to be a sesquibasic salt, composed of

					Phillips.		Klaproth. Vauquelin. Pelletier.								
					Native.	Artificial.	Native.	Native.	Artificial.						
Oxide of copper	3	...	120	...	69·37	...	69·08	...	67·6	...	70	...	68·75	...	59·7
Carbonic acid....	2	...	44	...	25·43	...	25·46	...	24·1	...	24	...	25·00	...	30·0
Water	1	...	9	...	5·20	...	5·46	...	5·9	...	6	...	6·25	...	3·3
Impurities									2·4						7·0

There is a very inferior pigment, also called *verditer*, which is a mixture of subsulphate of copper and chalk. According to Pelletier, a good verditer may be obtained as follows: Add a sufficient quantity of lime to nitrate of copper to throw down the hydrated oxide; it gives a greenish precipitate, which is to be washed and nearly dried upon a strainer; then incorporate with it from 8 to 10 *per cent.* of fresh lime, which will give it a blue color, and dry it carefully.

Native Carbonates of Copper. *Malachite*, or the *green hydrous carbonate*, $= 2\text{CuO}, \text{CO}_2, \text{HO}$, is found in various forms, but never regularly crystallized, the octohedral variety being a pseudo-crystal derived from the decomposition of the red oxide: it occurs in great beauty in the Uralian Mountains of Siberia; it is rarely found in Cornwall. It is of various shades of green, and often cut into small slabs, or used as beads and brooch-stones. The pulverulent variety has been termed *chrysocolla*, and *mountain-green*. The *blue hydrated carbonate* $= 3\text{CuO}, \text{CO}_2, \text{HO}$, is found in great perfection at Chessy, near Lyons: also in Bohemia, Saxony, &c. It occurs crystallized in rhomboids and imperfect octohedra; it is also found in small globular masses; massive; and earthy. The earthy variety is sometimes called *copper-azure* or *mountain-blue*. Graham represents this as a neutral hydrated carbonate of copper, combined with a similar carbonate, in which the constitutional water is replaced by oxide of copper: or as $= [\text{CuO}, \text{CO}_2 + \text{HO}] + [\text{CuO}, \text{CO}_2 + \text{CuO}]$. This is in fact the result of Phillips' analysis above quoted. The *Diopase*, or *Copper Emerald*, a very rare mineral, hitherto found only in Siberia associated with malachite, is a *hydrated silicate of copper*; some of the varieties of malachite also appear to contain a silicate of copper.

AMMONIO-CARBONATE OF COPPER. $\text{CuO}, \text{NH}_3, \text{CO}_2$. To a saturated solution of carbonate of copper in carbonate of ammonia add twice its volume of alcohol: after twelve hours the above compound separates in crystals resembling Chessy copper ore. When the residuary liquid is exposed to air, a bluish-green crystalline crust is formed $= 2\text{CuO}, \text{CO}_2, 2\text{HO}$. (FAVRE, *Journ. de Pharm.*, April, 1844.)

BORATE OF COPPER. Solution of borax, poured into sulphate of copper, produces a bulky pale-green precipitate of *borate of copper*, which fuses into an opaque green glass.

CYANIDES OF COPPER. Hydrocyanic acid and cyanide of potassium throw down a white curdy precipitate in the solution of dichloride of copper. A similar compound is obtained by the action of dilute hydrocyanic acid upon hydrated dioxide of copper: it is soluble in ammonia, and the solution is colorless; it is also soluble in hydrochloric acid and

precipitated by dilution, and by potassa: it combines with other metallic cyanides, forming a class of *cuprocyanides*. When hydrated oxide or carbonate of copper is digested in dilute hydrocyanic acid, a yellow powder is formed, insoluble in water, but soluble in hydrochloric acid and again precipitable by dilution.

CUPROCYANIDE OF POTASSIUM. Cyanide of copper, digested in a solution of cyanide of potassium, yields a yellow solution, from which small yellow transparent prismatic crystals (white acicular crystals, MEILLET, *Chem. Gaz.*, Aug., 1843) may be obtained, of a bitter metallic taste. This salt is not altered by the alkalis, but acids precipitate cyanide of copper from it, which excess of acid afterwards dissolves with the evolution of hydrocyanic acid. (ITTNER.) According to Gmelin, these crystals, if obtained from *oxide* (and not from dioxide) of copper, are a *cupro-dicyanide* of potassium; for during the solution of oxide of copper in cyanide of potassium, cyanogen is evolved, and the solution yields a white curdy precipitate of dicyanide of copper on the addition of hydrochloric acid. When a solution of this cuprocyanide is added to other metallic solutions, an interchange ensues between the potassium and the metal in the solution, and double cyanides are formed, in which one of the metals is always copper: the precipitate with *gold* is green; with *silver*, dark-brown; with protosalts of *iron*, greenish-yellow; with the persalts of iron the precipitate is only a mixture of cyanide of copper with peroxide of iron; with *lead*, pale-green; with *zinc*, *bismuth*, and *manganese*, pale-yellow. Acids decompose these precipitates, dissolving them and evolving hydrocyanic acid; the salts of *tin* yield mere mixtures of cyanide of copper and oxide of tin: the relative proportion of the copper to the other metals, in these compounds, has not been accurately determined. (BERZELIUS.) The solution of cyanide of copper in cyanide of potassium is recommended by Levol for coppering zinc by immersion, and by electric decomposition.

FERROCYANIDE OF COPPER is thrown down by ferrocyanide of potassium, from the solutions of oxide of copper, in the form of a beautiful brown powder, which has been used as a pigment; it is partially soluble in ammonia, insoluble in acids, and decomposed by caustic potassa. Cold concentrated sulphuric acid whitens it, but, on the addition of water it again becomes brown. Ferrocyanide of potassium is so delicate a test of the salts of copper, that it will distinctly detect 1 part of that metal in 60,000 of the solution. The only other metal which gives a precipitate resembling ferrocyanide of copper, is uranium.

SULPHOCYANIDE OF COPPER is formed by adding a solution of protosulphate of iron to a mixture of sulphate of copper and sulphocyanide of potassium: it falls as a white granular precipitate, insoluble in water. (LIEBIG.)

ALLOYS OF COPPER. Many of these compounds are of great use in the arts, especially those with zinc and tin, and with silver and gold; of these, the two latter will be noticed under those metals. The alloys of copper with *potassium* and *sodium* have not been particularly examined: Davy formed them, and ascertained that they decompose water. Berthier found in an extremely malleable copper, traces of

potassa and lime, together with a minute quantity of iron: Dumas states its composition as, copper 99·12; potassium 0·38; calcium 0·33; iron 0·17. He refers its remarkable malleability to the potassium, and suggests the addition of a small quantity of tartar to fused copper as a probable means of rendering it more malleable. *Manganese* was combined with copper by Bergman, and the properties of the alloy were examined by Gmelin. (*Göttingen Commentaries*, 1787.) *Iron* and copper combine with difficulty: 100 parts of grey cast-iron and 5 of copper yield a very hard alloy, of which Rinmann has proposed to make anvils. Steel is deteriorated by copper (FARADAY), and it renders cast-iron brittle (MUSHET). With *zinc* and *tin* copper forms brass and bronze. With *cadmium*, the alloy is brittle and harsh; it is decomposed by keeping it long in fusion, when the cadmium gradually volatilizes: at a red-heat, 100 of copper retain 82·2 of cadmium, so that this alloy is nearly =Cu2 Cd. The alloy of copper and *cobalt* has not been examined. With *nickel*, copper yields pakfong and German silver or argentan. According to Erdmann, a little copper destroys the magnetism of nickel, but the smallest quantity of iron restores it. Dumas gives the following view of the composition of different pakfongs. (See also TOPPING, p. 818.)

	For spoons and forks.		For knife- handles and snuffers.		For lamination.		For articles which require soldering.		White, but harsh and hard.		Chinese pakfong.
Copper	50	55	60	57	53	40·4
Nickel	25	22	20	20	22	31·6
Zinc	25	23	20	20	23	25·4
Lead	0	0	0	3	0	0·0
Iron	0	0	0	0	2	2·6
	<hr/> 100		<hr/> 100		<hr/> 100		<hr/> 100		<hr/> 100		<hr/> 100·0

German nickel is used by the manufacturers of pakfong: it is broken up and mixed with the granulated copper and zinc, taking care that copper forms the upper and lower stratum in the crucible: the whole is covered with charcoal-powder and fused in a wind furnace; it is stirred and kept for some time in fusion, at the risk of evaporating part of the zinc. When the clippings and filings are remelted, 3 or 4 *per cent.* of zinc are added to compensate for volatilization. This alloy has lately been much used for the manufacture of articles afterwards to be electro-plated.

BRASS. In making this important alloy of copper with zinc, the metals are usually united by mixing granulated copper with calamine and charcoal: the mixture is exposed to heat sufficient to reduce the calamine and melt the alloy, which is then cast into plates. The relative proportions of the two metals vary in the different kinds of brass; and some contain a little lead and tin. The composition of the principal varieties is shown in the following table: (DUMAS. *Chim. app. aux Arts*, III. 509.)

	For Turning.				For Gilding.				For Wire.	For Ham- mering.	For Fine Casting.				
Copper	61·6	...	65·8	...	63·7	...	82	...	66·5	...	70	...	91·2	...	91·7
Zinc ...	35·3	...	31·8	...	33·6	...	18	...	33·1	...	30	...	5·6	...	5·0
Lead ...	2·9	...	2·2	...	2·5	...	1	...	0·4	...	0	...	1·8	...	2·3
Tin.....	0·2	...	0·2	...	0·2	...	3	...	0·0	...	0	...	1·4	...	1·0
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	100·0		100·0		100·0		104		100·0		100		100·0		100·0

From the following tabular view of the composition of several varieties

of common brass, it would appear that it closely corresponds to the formula Cu_5,Zn_2 , which would give 71.43 copper + 28.57 zinc *per cent.*

	1	2	3	4	5	6	7	8	9
Cu	715 710 714 719 703 702 700 658 616
Zn	285 276 282 277 293 275 300 318 353
Sn trace 8 2 8 3 3
Pb 13 3 2 21 29
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1000	999	996	1004	1001	987	1000	1000	1001

Collins' and Muntz's patent sheathing metal, which has been found an excellent substitute for copper, is an alloy of about 60 copper and 40 zinc: it admits of being rolled hot, whereas the common varieties of brass generally split under such circumstances, and are therefore rolled cold, which requires more time.

Brass is very malleable and ductile (when cold), and its color and little liability to rust recommend it in preference to copper for many purposes of the arts: its specific gravity varies from 7.9 to 8.9, and exceeds the mean of its components, as shown by the following results. (DUMAS.)

	Copper.		Zinc.		Actual Density.		Calculated Density.	
I.	70	30	8.443	8.390	
II.	80	20	8.940	8.560	

According to Regnault, the specific heat of a brass composed of 71 copper, 27.6 zinc, and 1.3 lead, and affording traces of tin, is 0.09391. (*Ann. Ch. et Ph.*, Lxxiii. 33.) According to Sage, a beautiful brass may be made by mixing 50 parts of oxide of copper, 100 of calamine, 400 of black flux, and 30 of charcoal powder; melt these in a crucible till the blue flame is no longer seen round the cover; and, when cold, a button of brass is found at the bottom, of a golden color, and weighing one-sixth more than the pure copper obtained from the above quantity of oxide. The presence of iron and of tin in brass should be carefully avoided, where they may interfere with its ductility or malleability, or where magnetic apparatus is concerned.

Tutenag is an alloy of copper, zinc, and a little iron (and nickel, according to Topping: see p. 818): *Tombac*, *Dutch Gold*, *Similor*, *Prince Rupert's Metal*, and *Pinchbeck*, are alloys containing more copper than exists in brass, and consequently made by fusing various proportions of copper with brass. According to Wiegleb, *Manheim Gold* consists of 3 parts of copper and 1 of zinc. A little tin is sometimes added, which, though it may improve the color, impairs the malleability of the alloy. An alloy of 576 parts of copper, 59 of tin, and 48 of brass, is equal to brass in hardness, and may be worked with the same facility; it was used by Bate for the new standard measures, as being less liable than brass to oxidizement. (*Phil. Trans.*, 1826.) Brass is *reddened* when rubbed over with hydrochloric acid, but *whitened* with ammonia; the former abstracting zinc, the latter copper, from the surface of the alloy.

According to Karsten, alloys which contain less than 50 *per cent.* of zinc, act towards acids, and in the simple voltaic circle, as copper, and do not decompose copper salts; but where the zinc exceeds 50 *per cent.*, the alloy, when immersed in solutions of copper, decomposes them, and becomes pure copper. (In reference to the mechanical properties of the varieties of brass, see MALLET, *Trans. Soc. Civil Engineers.*)

Speculum Metal is an alloy of copper and tin, with a little arsenic:

about 6 copper, 2 tin, 1 arsenic. On this subject the reader is referred to Edwards's experiments. (*Nicholson's Journal*, 4to., iii.) Little recommends 32 parts of best bar copper, 4 of brass pin-wire, $16\frac{1}{2}$ of tin, and $1\frac{1}{4}$ of arsenic. The Earl of Rosse (Lord Oxmantown) employed copper and tin only, in construction of the speculum of his enormous telescope; the proportions he used were 126·4 of copper, to 58·9 of tin, (about 4 atoms of copper to 1 of tin): this alloy was made and cast under many precautions. (See *Phil. Trans.*, 1840, p. 503.)

BRONZE. BELL-METAL. These are alloys of copper and tin; they are harder and more fusible, but less malleable, than copper. The specific gravity of bronze exceeds the mean of its component metals, when carefully hammered and free from air-blebs: but bronze castings are apt to be more or less porous and vesicular, unless considerable care and skill have been used in fusing and pouring the metal, and in the construction of the mould; and in large castings, owing to the gradual cooling of the mass, there is often a want of uniformity in the composition of different parts of it; that portion containing the least tin being the first to solidify, while the more fusible portion to a certain extent separates, and is sometimes projected from the mould. The following table, from the experiments of Briche, shows the actual and calculated density of different alloys of copper and tin. (*Journ. des Mines*, v. In reference to the other mechanical properties of the alloys of copper, such as color, fracture, cohesion, malleability, and hardness, see MALLET.)

Copper.	Tin.	Actual Density.	Calculated Density.	Difference.
100	4	8·79	8·74	0·05
100	6	8·78	8·71	0·07
100	8	8·76	8·68	0·08
100	10	8·76	8·66	0·10
100	12	8·80	8·63	0·17
100	14	8·81	8·61	0·20
100	16	8·87	8·60	0·27
100	33	8·83	8·43	0·40
100	100	8·79	8·05	0·74

In large bronze castings, such as statues, porosity and bubbles require carefully to be avoided; where they exist so as to deface the appearance of the work, they are sometimes filled up with substances which are only temporarily durable, or which, if metallic, give rise to electrical effects which time must render prejudicially evident: for this reason also, the different pieces of a large statue should be fused together, or united by bronze, and not by a mere fusible solder; and iron bars, and leaden junctions for the support or fixing of the work, should, upon the same principle, be avoided, as they are themselves liable, under such circumstances, to corrosion, and this may affect the stability, or safety of the statue, independent of other influences.

When bronze is frequently remelted it gradually loses tin by oxidizement, so that in such cases fresh additions of tin may sometimes be requisite; and it is apparently this oxidizement of the tin which tends to deteriorate the texture of remelted bronzes, and renders them more subject to bubbles and porosity when recast, an effect which may be prevented by the action of carbonaceous fluxes, or by the operation of poling, as in the case of copper.

Tempering produces upon bronze an effect directly opposite to that upon steel*; and in order to render bronze malleable, or fit for the coining press, it must be heated to redness and quenched in water: the alloy which thus acquires the greatest tenacity is that of 8 of copper and 1 of tin, and this is consequently preferable for medals; the advantage of bronze over copper for these purposes being hardness, and resistance to oxidizement; the former quality resists friction, and the latter has handed down to us the works of the ancients with little deterioration, though buried for ages in damp soil, or immersed in water: the small value of bronze, too, as compared with gold and silver, is another important consideration, as affecting the preservation of such works of art. The following are the component parts of the different bronzes and bell-metals in common use.

Common use.		For Coin and Medals.		Gongs and Cymbals.		Gun-metal. Statues and Large Castings.		Bell-metal.					
Copper	93	89	78	92	89	80	83
Tin	7	11	22	8	11	10	17
Zinc	0	0	0	0	0	6	0
Lead	0	0	0	0	0	4	0
	<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>		<hr/>
	100		100		100		100		100		100		100

The analysis of brass may be performed, (1.) by solution in nitric acid; then add considerable excess of solution of potassa, and boil, which will dissolve the oxide of zinc and leave that of copper; wash the latter, and dry and heat it to redness: 100 parts indicate 80 of copper. The zinc in the filtered alkaline solution may be precipitated by carbonate of soda, having previously added a small excess of hydrochloric acid; wash this precipitate, dry it, and expose it to a red heat; it is then oxide of zinc, 100 parts of which also indicate 80 of metal. (2.) But as, in this process, the whole of the oxide of zinc is not easily removed by the alkaline solution, Keates recommends the following as preferable: Dissolve 100 grains of the brass in dilute nitric acid, evaporate to dryness, and redissolve in excess of dilute sulphuric acid; filter, to separate sulphate of lead, if any be present; dilute the solution, heat it to its boiling-point, and introduce three polished cylinders of iron, each about an inch long and a fourth of an inch diameter; continue the boiling till the solution becomes colorless, and when tested by a clean plate of iron shows no trace of copper. Filter the solution while hot, and wash the precipitated copper first with very dilute sulphuric acid, and afterwards with boiling water; dry it, and fuse it into a button in a crucible covered with charcoal-powder. Boil the filtered solution with the addition of some nitric acid to peroxidize the iron, and nearly neutralize by carbonate of soda; then add excess of ammonia, to throw down the peroxide of iron, which separate by filtration. Add hydrochloric acid to the filtered ammoniacal solution, evaporate to dryness, and heat in a silver crucible to drive off hydrochlorate of ammonia; dissolve the residue in hydrochloric acid, and precipitate by excess of carbonate of soda; wash, dry, and ignite the precipitate, which reduces it to the state of oxide of zinc. (3.) Dissolve

* Regnault found the specific heat of a | softened by tempering, 0·0862. The spe-
bronze composed of 80 copper, 20 tin, in | cific gravity of the former was 8·579, and
its ordinary state to be 0·0858, and when | of the latter 8·634.

in nitric acid; test for lead by sulphuric acid; if absent, dilute the acid solution, and precipitate the copper by a stream of sulphuretted hydrogen; filter; and boil, to expel sulphuretted hydrogen. Digest the washed sulphuret of copper remaining upon the filter, in nitric acid, and when dissolved precipitate the copper by potassa; wash, dry, and ignite the precipitate, and weigh it as oxide. The zinc may be obtained also as oxide, by evaporating the filtered solution, and calcining the residuary nitrate of zinc in a platinum crucible.

The analysis of alloys of tin and copper may be performed by digestion in nitric acid, which dissolves the copper and converts the tin into insoluble peroxide, which, when washed and dried, consists of 78·7 tin + 21·3 oxygen. The cupreous solution may be decomposed by potassa, and the oxide of copper indicates the quantity of that metal, as in the analysis of brass.

Tinned Copper. Vessels of copper used for culinary purposes are usually coated with tin, to prevent the food being contaminated with copper. Their interior surface is first cleaned, then rubbed over with sal-ammoniac. The vessel is then heated, a little pitch spread over the surface, and a bit of tin rubbed over it, which instantly unites with and covers the copper. Much care is requisite in the manipulations of this process, and independent of the tin permanently adhering to and combined with the surface of the copper, there is generally a portion in excess which fuses off the first time the pan is used for frying or melting fat or butter; lead is sometimes added to the tin used in tinning, and sometimes a small quantity of mercury: it appears from Proust's detailed experiments on this subject, that the small quantity of lead thus employed can scarcely be regarded as prejudicial, and that as respects the action of acids in such cases, the tin is dissolved before the lead; the use of mercury is more objectionable.

CHARACTERS OF THE SALTS OF COPPER. The cupreous salts are nearly all soluble in water, and of a blue or green color. Ammonia produces a compound of a very deep blue, when added in excess to these solutions; solutions of nickel give a similar color, but the ammoniated solutions of nickel are easily distinguished by the other tests, from the corresponding cupreous combinations; hydrosulphuret of ammonia forms a black precipitate. Ferrocyanide of potassium is also an excellent test of the presence of copper (in the absence of uranium;) it produces a brown cloud in solutions containing the minutest portion of the oxide; in this way the presence of an extremely minute trace of metallic copper in solution may be detected, (provided the color of the vehicle does not interfere,) by a reddish-brown cloud, which appears in a moment or two after the application of the test*.

* Mr. Alfred Taylor gives me the following caution in reference to the use of this test in organic solutions:—"In April, 1838, I examined the contents of the stomach of a person poisoned by oxalic acid: a tolerably clear liquid was obtained by boiling and filtration, and oxalic acid was easily detected. On adding solution of ferrocyanide of potassium to a portion of the liquid, a deep claret-colored pre-

cipitate fell exactly like ferrocyanide of copper. I immediately tried the liquid with polished iron and ammonia, but could find no trace of copper; the liquid was faintly acid, and after having been kept for some days, no effect was produced by the ferrocyanide; I can only ascribe this anomalous result, to the presence of some peculiar organic compound."

The metallic precipitation of copper from its solutions is effected by zinc, iron, cadmium, tin, lead, and cobalt, and, under certain circumstances, feebly by bismuth. The copper sometimes appears in a clean metallic state, but is frequently alloyed by or blended with the precipitating metal, or mixed with other products. The different salts of copper are in this way differently affected. *Nitrate of copper*, for instance, is reduced by zinc, lead, cadmium, and tin, but when quite neutral, and out of the contact of air, iron very imperfectly and slowly acts upon it. In a common acid solution of the nitrate a plate of iron becomes immediately covered with copper. Cobalt acts very slowly, and bismuth only when heated in the solution, and then imperfectly. The reduced copper appears with its metallic lustre and peculiar color, only upon cobalt, lead, and iron; with the other metals it forms a coating of a brown or black color. With tin, the oxide of that metal is also precipitated. *Sulphate of copper* is reduced by the other metals much in the same way as the nitrate: iron first becomes covered by pure copper, after which the formation of a subsalt of iron gives it a brown color. The action of lead upon solution of sulphate of copper is very feeble; cobalt acts rapidly, and becomes coated with clean copper. The precipitate upon tin is accompanied by sulphate of tin, in the form of a white shining powder, but if air be excluded, protosulphate of tin remains in the solution, with a portion of sulphate of copper: in such cases the whole of the copper is never separated. *Chloride of copper* is easily decomposed by iron, tin, zinc, cadmium, and cobalt, and slowly by lead, provided the solution be not acid. *The ammoniacal solution of oxide of copper* is only reduced by zinc, iron, and cadmium, not by tin, lead, or cobalt. Zinc is by far the most effectual precipitant of copper. When the metallic precipitation of copper is resorted to for the detection of minute quantities of the metal, as for instance in cases of poisoning, iron is the preferable precipitant, and when carefully used, gives very delicate indications, and is applicable in certain cases where the other tests are interfered with by the color of the contaminated vehicles, such as beer, wine, soup, the contents of the stomach, &c. Mr. Taylor informs me that he has in this way detected copper in gruel and the liquids just mentioned, when only 1 grain of crystallized sulphate of copper was present in 12 ounces of the liquid, and when the test by ferrocyanide of potassium was inapplicable from the color of the vehicle. He finds the most delicate mode of applying this test is to render the suspected liquid very slightly acid by a drop or two of dilute sulphuric acid, and then to suspend it in a clean sewing-needle; in a day or two the coating of copper becomes perceptible. When insoluble salts are thus examined, they may be moistened with dilute sulphuric acid, and rubbed upon polished iron.

The voltaic precipitation of copper is also often conveniently applicable to the detection of this metal; a few drops of the suspected liquid may be put upon clean platinum foil and touched by a wire of zinc, when a film of copper immediately coats the platinum. (In reference to this precipitation of copper for electrotypes, &c., see p. 220; also SMEE, *Electrometallurgy*. WALKER, *Manual of Electricity*, &c., II. 366, and the authorities which he cites.)

Before the *blow-pipe* oxide of copper is not altered by the exterior flame, but becomes suboxide in the interior. With both microcosmic salt

and borax it forms a yellow-green glass while hot, but which becomes blue-green as it cools. When strongly heated in the interior flame, it loses its color, and the metal is reduced. If the quantity of oxide be so small that the color is not perceptible, its presence may be detected by the addition of a little tin, which occasions a reduction of the oxide to sub-oxide, and produces an opaque red glass. If the oxide has been fused with borax, this color is longer preserved; but if with microcosmic salt, it soon disappears by a continuance of heat. The copper may also be precipitated upon iron, but the glass must be first saturated with iron. Alkalis or lime promote this precipitation. If the glass, containing copper, be exposed to a smoky flame, the copper is superficially reduced, and the glass covered while hot with an iridescent pellicle, which is not always permanent after cooling. It is very easily reduced by soda. Salts of copper, when heated before the blow-pipe, give a fine green flame.

It has already been remarked that the presence of organic substances in solutions of copper materially interferes in some cases with the action of reagents, and as, in consequence of the use of copper vessels for culinary purposes, the contamination of food by this poisonous metal is not uncommon, it often requires minute attention in judicial inquiries. (See CHRISTISON on *Poisons*, Art. *Copper*; A. TAYLOR, *Medical Jurisprudence*, ch. xx.; ROSE'S *Analytical Chemistry*.) In these cases precipitation by iron may, as above stated, be resorted to: or the suspected articles may be evaporated to dryness, carefully incinerated, and the residue treated by a little nitric acid: in this way a solution of nitrate of copper is obtained, to which the ordinary tests, under the precautions above pointed out, may be applied.

COPPER COINAGE. The following table shows the standard weights, value, &c., of the copper coins of Great Britain.

COPPER COINS. Standard Weights; Remedy; Legal Tender, &c.

Denomination of coin.	No. of pieces in the lb. avoird.	Weight of each piece.		Value of one lb.	No. of pieces in a ton.	Value of a ton.	Remedy by Indenture.	Legal tender.	Date of proclamations fixing the amount of legal tender.	Where current.
		In drs. avoird.	In troy grains.							
Pence	24	10·66	291·66	s. 2	53,760	£ 224	$\frac{1}{40}$ or six	12	14 Nov. 1821,	United Kingdom, and British Cols.
Half-pence ..	48	5·33	145·83	2	107,520	224	drms. and	6	and	
Farthings	96	2·66	72·91	2	215,040	224	$\frac{4}{10}$ avoird.,	6	30 Jan. 1826.	
$\frac{1}{2}$ do	192	1·33	36·45	2	430,080	224	or 175 tr.	Ceylon.
$\frac{1}{10}$ of a penny	240	1·06	29·16	2	537,600	224	grns. per	Ionian Islands
$\frac{1}{3}$ of farthing	288	·88	24·30	2	645,120	224	lb. avoird.	Malta.
$\frac{1}{4}$ do	384	·66	18·22	2	860,160	224	dupois.	Ceylon.

The moneymen deliver the coined moneys to the Mint office in bags containing $\frac{1}{2}$ cwt. avoirdupois, in value £5 12s. 0d. The deliveries to the public are made in bags of 50 lbs. weight avoirdupois, value £5.

§ XVI. LEAD. Pb. 104.

LEAD has been known from the earliest ages of the world. The alchemists gave it the symbol and name of Saturn, h_2 . It is said to occur *native* in the lava of Madeira and of some other volcanic districts; also in a variety of galena at Alston in Cumberland, and in the carboniferous limestone of the county of Kerry in Ireland, and in the vicinity of Bristol. (AUSTIN, *Phil. Mag.*, March, 1843.) The native compounds of lead are very numerous: the most important is the *sulphuret*, from which the pure metal is chiefly procured. Lead is also found combined with carbonic, sulphuric, phosphoric, arsenic, molybdic, and chromic acids, and with oxygen and chlorine.

Perfectly pure lead may be obtained,—1, by reducing pure nitrate of lead by charcoal, at a red heat, in an earthen crucible. 2. By heating oxalate of lead in a covered crucible. Its color is bluish-white; it has much brilliancy, is remarkably flexible and soft, and leaves a black streak on paper: when handled it exhales a peculiar odor. It admits of being rolled into thin sheets, and drawn into moderately-fine wire, but its tenacity is so low, as to render the latter operation difficult. It melts at about 612° , and, by the united action of heat and air, is readily oxidized: in perfectly close vessels it does not sublime at a bright red-heat; but before the oxygen blow-pipe it boils when heated to whiteness, and is dissipated in copious fumes of oxide. Its specific gravity, when pure, is 11.445, but the lead of commerce seldom exceeds 11.35. Its specific heat, according to Regnault, is 0.03140. When slowly cooled it forms octohedral crystals, and contracts considerably during its solidification; in bullets, therefore, and in castings of lead rapidly cooled, there is generally a cavity which, in rifle shooting, interferes with the rectilinear passage of the ball, so that for such purposes the balls are sometimes moulded out of rolled lead. The specific gravity of lead is said not to be increased by hammering, for although it becomes hot during that operation, it at the same time acquires fissures.

At common temperatures, and in its ordinary state, lead undergoes little change by mere exposure to air; but when in a state of very fine division, as it is obtained diffused through charcoal, by exposing *tartrate of lead* to a red-heat in close vessels, it takes fire when brought into the contact of air; so also the finely-divided lead obtained by the reduction of the oxide by hydrogen at a temperature insufficient for its fusion, burns when gently heated in the air. In distilled water, free from air and in close vessels, a clean surface of lead remains bright; but, under the same circumstances, in open vessels, it soon tarnishes, and small crystalline scales of hydrated oxide of lead are formed, a portion of which dissolves in the water, and is again slowly precipitated in the form of subcarbonate. (YORKE, *Phil. Mag.*, August, 1834.) In this case the oxygen is imparted by the air held in solution in the water; the film of oxide thus formed is soluble to a small extent in the pure water, and is thrown down in proportion as it passes into the state of carbonate. Christison has observed, that the compound of lead which is formed in these cases is frequently crystalline, and therefore probably of definite composition; and on examining it in this state, he found it to be a hydrated oxycarbonate represented by the formula $3\text{PbO} + 2\text{CO}_2 + \text{HO}$. On

filtering this contaminated water, the greater part of the lead is retained by the fibres of the paper. (YORKE, *Mem. Chem. Soc.*, II., 399.) A very minute trace of sulphuric acid, or of a soluble sulphate, in the water, prevents this continuous corrosive effect, and hence it is that common river and spring water is kept with considerable impunity in leaden cisterns, which, however, should have *wooden* and not leaden covers; in the latter case, the vapor of the water below condenses upon the cover, and often tends to its corrosion, it being in fact distilled water, and not therefore prevented in its action by saline matters. Where spring water is extremely free from saline substances, or only contains such as do not in very small quantity furnish a protective coating; or where rain water is preserved in lead, and where, consequently, poisonous effects might be apprehended from its use, the pipes and cisterns may be filled with a very weak solution of phosphate of soda, by which they will become so covered by an insoluble film as to resist further action. Dr. Christison says that he successfully resorted to this expedient in a case detailed in the *Edinb. Phil. Trans.* (XV., 271,) to which he adds the following remarks: "1. Lead pipes ought not to be used without a chemical examination of the water to be transmitted. 2. The risk of dangerous impregnation is greatest in the purest waters. 3. Water which tarnishes polished lead, when left in contact with it for a few hours, cannot be safely transmitted through lead pipes without certain precautions. 4. Water containing less than an 8000th of salts in solution cannot be safely conducted in lead without certain precautions. 5. Even this proportion will prove insufficient to prevent corrosion, unless a considerable part of the saline matter consist of carbonates and sulphates, especially the former. 6. So large a proportion as a 4000th will be insufficient, if the salts be chiefly chlorides." Another source of contamination by lead may arise from electric action, as where iron or copper bars, screws, or pipes, are in contact with or soldered into lead: and in these cases, owing to the action of alkaline bases as well as of acids upon the lead, danger may occur when it is thrown into an electro-negative as well as electro-positive state. Cisterns are sometimes corroded, and holes eaten through their bottoms by pieces of mortar having dropped into them, the lime of which has tended to oxidize the metal, and dissolve the oxide. The means of detecting lead are fortunately simple and delicate, as will appear from the sequel. The equivalent of lead is 104. (104 GMELIN: 103.56 BERZELIUS: 103.6 TURNER: 103.73 GRAHAM.)

OXIDES OF LEAD. There appear to be five definite combinations of lead and oxygen, namely a *dioxide* or *suboxide*, Pb_2O ; a *protoxide*, PbO ; an intermediate oxide generally known as *red oxide*, Pb_3O_4 ; a *sesquioxide* Pb_2O_3 ; and a *peroxide*, PbO_2 . Of these oxides, the protoxide only is salifiable.

DIOXIDE OF LEAD. SUBOXIDE OF LEAD. Pb_2O . When *oxalate of lead* is carefully heated in a fusible metal bath to about 570° in a small retort, carbonic oxide and carbonic acid are evolved, and a dark-grey powder remains, which is resolved by acids into protoxide and metallic lead, and which, according to Dulong, is a definite suboxide. The grey powder with which lead that has been long exposed to air, especially if heated, becomes covered, is, according to Berzelius, similar in composition.

Boussingault found that mercury triturated under water with this oxide, abstracts no lead from it, and therefore infers that it is not a mixture of metallic lead with the protoxide, notwithstanding its resolution into such a mixture by acids. (*Ann. Ch. et Ph.*, liv. 264.) The decomposition of oxalate of lead has been carefully and accurately investigated by Pelouze. (*Ann. Ch. et Ph.*, 3 Ser. iv. 108.) He finds the products vary with the temperature, but if this be maintained at about 570° (300° Cent.) carbonic acid and carbonic oxide, in the relative proportions of 3 to 1, are evolved, and a true suboxide or dioxide of lead remains: that is, 2 equivalents of oxalate of lead yield 1 of dioxide, 3 of carbonic acid, and 1 of carbonic oxide, or $2[\text{PbO}, \text{C}_2\text{O}_3] = \text{Pb}_2\text{O} + 3\text{CO}_2 = \text{CO}$.

Dioxide of lead is a black powder, upon which at common temperatures mercury has no action: it contains no protoxide of lead, for when boiled out of the contact of air with sugar (which readily dissolves the protoxide) nothing is taken up. Nitric, sulphuric, hydrochloric, and acetic acids resolve it into finely-divided metallic lead and protoxide. The soluble alkalis produce a similar change, so also does nitrate of lead; in a weak solution of this salt the dioxide gradually disappears, and the boiling filtered solution deposits a mixture of nitrate, and basic nitrate of lead. Moistened and exposed to air, this dioxide heats and becomes white, passing into hydrated protoxide: at a dull red-heat it decomposes into a mixture of lead and protoxide. The components of this oxide are

Lead	2	208	96.3
Oxygen	1	8	3.7
<hr/>					
Dioxide of lead	1		216		100.0

PROTOXIDE OF LEAD, PbO , is formed, (1.) by raising the temperature of melted lead to a white-heat, when it burns with a brilliant flame, and forms copious fumes of protoxide. (2.) By exposing the grey powder which gradually collects upon the surface of melted lead, to the further action of heat and air till it acquires an uniform yellow color. (3.) By exposing pure nitrate, or subnitrate, or carbonate of lead, to a dull red-heat out of contact of air, and taking care to avoid fusion. (4.) When a solution of acetate of lead is dropped into a solution of ammonia, the white powder which falls is a *hydrated oxide*, which examined by a microscope, is in the form of small prismatic crystals. Payen obtained this hydrated oxide, together with crystals of anhydrous protoxide, by decomposing tribasic acetate of lead by ammonia. (*Ann. Ch. et Ph.*, lxvi. 54.) When this oxide is heated it has a red color, but in its ordinary state it is lemon or orange-yellow, according to the mode in which it has been prepared, and is known under the name of *Massicot*. At a high red-heat it fuses, and forms, on cooling, a lamellar vitreous mass of a reddish-brown color: this is often obtained in scales, under the name of *Litharge*, which, when of a red color from the presence of minium, was called *Litharge of Gold*, the paler varieties being termed *Litharge of Silver*. When of a dark hue from the presence of a little sulphuret of antimony, these vitrified oxides are known by the German term *Abstrich*.

Protoxide of lead is a salifiable base, forming neutral salts with the acids; and, in many instances, subsalts, which have an alkaline reaction;

when moist or in the state of hydrate, (and even when dry, according to Berzelius,) it absorbs carbonic acid from the atmosphere, and gradually acquires the property of dissolving in acids with effervescence. It is soluble in potassa and soda, forming yellow liquids, which after a time gradually deposit micaceous or dodecahedral crystals of anhydrous oxide of lead, probably in consequence of the slow absorption of carbonic acid by the alkali; it combines with baryta, strontia, and lime, forming compounds of sparing solubility, and easily decomposed even by the weakest acids: a paste or wash, containing hydrate of lime and oxide of lead, is used to blacken hair, which it does in consequence of the formation of a black sulphuret arising out of the combination of the sulphur in the hair with the metal of the oxide, while the lime by uniting with the oily matter facilitates the effect.

When oxide of lead is fused with the earths and metallic oxides, it forms vitreous and in some cases very fusible compounds, hence its use in the manufacture of glass; hence also the readiness with which it corrodes common crucibles when it is kept for a sufficient time in fusion in them. Heated with charcoal, this and the other oxides of lead are easily reduced to the state of metal; they are also reduced, when heated in hydrogen or coal gas. This oxide consists of

Dübereiner. Vauquelin. J. Davy. Proust. Richter.									
Lead.....	1	104	92.857	93.02	93	92.85	91	88.5	
Oxygen	1	8	7.143	6.98	7	7.15	9	11.5	
Protoxide of lead	1	112	100.000	100.00	100	100.00	100	100.0	

The hydrated oxide, when dried at about 100° , is a soft crystalline powder $= 3\text{PbO}, \text{HO}$: it is slightly soluble in pure water, and the solution has an alkaline reaction; it loses water, and gradually becomes anhydrous when heated to about 160° . The influence of carbonic acid and minute portions of saline substances upon the solubility of this hydrate, has already been noticed. It consists of

Mitscherlich. Payen.							
Protoxide of lead	3	336	97.39	96.5	97.35		
Water	1	9	2.61	3.5	2.65		
Hydrate of protoxide of lead	1	345	100.00	100.0	100.0		

RED OXIDE OF LEAD. MINIMUM. RED LEAD. Pb_3O_4 . This substance, which is well known as a common red pigment of a sp. gr. between 8.6, and 9, is made by exposing protoxide of lead to the action of heat and air, so as to oxidize, without fusing it, the temperature required for this purpose being between 570° and 580° ; it gradually acquires a fine red color, the splendor of which, however, goes off by exposure to light. To obtain it of a brilliant color it requires to be made in large quantities and with several precautions: the method formerly employed in Derbyshire is described in WATSON'S *Chemical Essays*. This oxide is not salifiable, but the acids convert it into protoxide and peroxide; they combine with the former, and leave the latter in the form of an insoluble brown powder; so that red lead may be considered as a compound of protoxide and peroxide (or a *diplobate of lead*) $= 2\text{PbO}, \text{PbO}_2$. The minimum of commerce is, however, of variable composition, and generally contains excess of protoxide, which may be separated by very dilute acetic acid, (PHILLIPS,) or better, according to Dumas, (*Ann. Ch. et Ph.*

XLIX.) by digestion in solution of acetate of lead. It is not easily made upon a small scale, but Fremy and Levöl obtained it in the humid way, by precipitating a hot solution of protoxide of lead in potassa, by peroxide of lead. (*Ann. Ch. et Ph.*, LXXV.) When exposed to a temperature somewhat above that required for its formation, minium gives off oxygen, and reverts to the state of protoxide: it was thus originally used as a source of oxygen gas by Priestley. The most perfect and brilliant minium as respects color, is said to be obtained by heating and stirring pure carbonate of lead in a current of air at a temperature a little short of 600°.

Minium, as above stated, is easily decomposed by the acids; thus nitric acid resolves it readily into insoluble peroxide, while a soluble nitrate of the protoxide is at the same time formed. Hydrochloric acid, in small quantity, (2 atoms to 1 of minium,) produces with it chloride and peroxide of lead, and water. $Pb_3O_4 + 2HCl = 3PbCl + PbO_2 + 2HO$: in larger quantity the products are chloride of lead, water, and free chlorine; $Pb_3O_4 + 4HCl = 3PbCl + 4HO + Cl$. With an aqueous solution of chlorine it affords chloride and peroxide of lead. $Pb_3O_4 + Cl = PbCl + 2PbO_2$. The components of minium may be represented by either of the following formulæ :

Lead 3....312....90·7	or { Protoxide 2....224....65·12 }	or { Protoxide 1....112....32·56 }
Oxygen 4.... 32.... 9·3	= { Peroxide 1....120....34·88 }	= { Sesquioxide 1....232....67·44 }
<hr/>		
Pb_3O_4344 100·0	$2PbO, PbO_2$ 344 100·00	PbO, Pb_2O_3 344 100·00

SESQUIOXIDE OF LEAD. Pb_2O_3 . Chloride of soda, added to solutions of the salts of lead, throws down an orange-colored precipitate, which is a mixture of sesquioxide and chloride of lead: to obtain this oxide free from chloride, add excess of potassa to nitrate of lead so as to redissolve the precipitated hydrated oxide; then precipitate by chloride of soda, wash the precipitate, and dry it in vacuo over sulphuric acid. It is an orange-colored crystalline powder, resolved by a red-heat into 3·5 *per cent.* oxygen and 96·5 protoxide: with nitric acid it yields a protonitrate and peroxide; and with hydrochloric acid, chlorine and chloride of lead. (*WINKELBLECH, Ann. der Pharm.*, xxi.) Its components are

						Winkelblech.
Lead.....	2	208	89·66 89·64
Oxygen	3	24	10·34 10·36
<hr/>						<hr/>
Sesquioxide of lead.....	1		232		100·00	100·00

PEROXIDE OF LEAD. BINOXIDE OF LEAD. PLUMBIC ACID. PbO_2 . This oxide is obtained in the form of an insoluble brown powder by digesting minium in cold nitric acid; or by heating salts of lead with chloride of soda; or by passing chlorine through minium diffused in water, or through a solution of acetate of lead, and thoroughly washing the product in hot water to remove the chloride of lead: the first is the best process, if the minium and nitric acid be pure; the resulting oxide only requires to be boiled in very dilute nitric acid, then well washed, and dried at 212°.

This oxide is an excellent conductor of electricity. (*FARADAY.*) At a red-heat it gives off oxygen, and is converted into protoxide. By the continued action of light or of a gentle heat it is resolved into oxygen and minium. Digested in liquid ammonia, a mutual decomposition takes place, and water and nitrate of lead are formed. Triturated with a fifth

of its weight of sulphur, it inflames spontaneously; or with half its weight of sulphur when touched with oil of vitriol. It is also decomposed with the evolution of heat when rubbed with an eighth of its weight of sugar; or with its weight of crystallized oxalic acid, with which it forms water, carbonic acid, and carbonate of lead. With hydrochloric acid, it furnishes chlorine and chloride of lead. When boiled in nitric or sulphuric acid, oxygen is evolved and salts of the protoxide are formed. It absorbs sulphurous acid gas with the evolution of much heat, or even with ignition, and forms sulphate of lead; hence its occasional use in the analysis of gaseous mixtures, to separate sulphurous from carbonic acid gas. It consists of

						Berzelius.
Lead.....	1	104	86.67 86.51
Oxygen	2	16	13.33 13.49
<hr/>						<hr/>
Peroxide of lead	1		120		100.00	100.00

PLUMBATE OF POTASSA. When potassa, moistened with a little water, and peroxide of lead are heated for a short time in a silver crucible, a compound is obtained which, dissolved in a small proportion of water and slowly evaporated, yields transparent crystals = $\text{KO}, \text{PbO}_2, 3\text{HO}$: they are deliquescent rhomboids, soluble without decomposition in solution of potassa, but resolved by pure water into hydrated peroxide of lead, and a brown solution of *biplumbate of potassa*. **PLUMBATE OF SODA** may be obtained in the same way, but it is little soluble in water. The insoluble plumbates are formed by heating mixtures of the bases with protoxide of lead, in the air, when oxygen is absorbed. *Plumbate of lime* and of *baryta* are so formed. (FREMY, *Ann. Ch. et Ph.*, Dec. 1844, p. 490.) Under this aspect minium is a plumbate of lead, = PbO, PbO_2 .

Metallo-chromes. When solutions of the salts of lead are electrolysed, they deposit its peroxide on the positive electrode. When *thin films* of peroxide of lead are thus formed by electrolytic action upon polished steel-plates, they give rise to those beautiful prismatic tints which Nobili originally described under the above name: the most perfect specimens which I have seen in this country were produced by Mr. Gassiot, to whom I am indebted for the following memorandum upon the subject. "Into a clear saturated solution of acetate of lead place a bright polished steel-plate, and on this a piece of thick card-board, out of which the required figure has been cut; a ring of wood of the size of the figure is then placed on the card, on which rests a copper disc, slightly concave, or convex, according as you may require the different colors: connect the positive electrode of a voltaic battery (I generally used three or four of Daniell's cells) with the steel-plate, and the negative with the copper disc. The beauty of the figure will depend on the energy of the battery, the strength of the solution, and the time employed; but, as above, from six to fifteen seconds is sufficient. Instead of the card and copper disc, I sometimes use negative electrodes composed of copper wire in different forms; the colors then overlap each other with their gorgeous tints in the most beautiful manner. The ultimate size of the figure is dependent upon that of the elements used; for instance, in attempting to make a figure of about eighteen to twenty inches diameter, I found it requisite to combine two or more zincs and two or more coppers together; the *size* of the figure depending on the *quantity*, and the *rapidity* of its production on the

intensity of the electricity and approximation of the electrodes, that is, of steel-plate and copper disc." (A notice of these experiments will be found in the *Proceedings of the Royal Society*, March, 1840.)

CHLORIDE OF LEAD. PbCl . When laminated lead is heated in chlorine, the gas is absorbed, and a *chloride of lead* results. (J. DAVY, *Phil. Trans.*, 1812.) The same substance is obtained by adding hydrochloric acid, or a solution of chloride of sodium, to a concentrated solution of nitrate of lead, washing the precipitate in cold water, and drying at 212° ; it is also formed when the oxides of lead are digested with heat, in hydrochloric acid. It is white and fusible, and, on cooling, forms a horn-like substance (*plumbum corneum*) of the specific gravity of 5.13. It does not absorb ammonia. (FARADAY.) It volatilizes at a high temperature, provided air has access, in which case a portion of oxide of lead is also formed. It is reduced by carbonic oxide at a red-heat, with the formation of chlorocarbonic acid. (GÖBEL.) It dissolves in 130 parts of water at 60° , but is much more soluble at 212° , separating, as its solution cools, in small anhydrous acicular crystals, unchanged by exposure to air, and of a sweetish taste. Its solubility in water is greatly diminished by the presence of a little hydrochloric acid, so that it is separated from water by the addition of that acid; yet it is very soluble in strong hydrochloric acid, and is precipitated on dilution. It dissolves rather copiously in solutions of the alkaline hyposulphites. (HERSCHEL.) It is insoluble in alcohol. Chloride of lead consists of

ide of lead consists of						J. Davy.	Döbereiner.		
Lead.....	1	104	74.3	74.22	75.758
Chlorine	1	36	25.7	25.78	24.242
<hr/>			<hr/>		<hr/>		<hr/>		<hr/>
Chloride of lead	1		140		100.0		100.00		100.000

Native Chloride of Lead occurs amongst the products of Vesuvius, in small acicular crystals: a *dichloride of lead*, Pb_2Cl , has been found in the Mendip-hills, in Somersetshire; it forms fibrous yellow crystalline masses upon a black ore of manganese; a *native oxichloride of lead* (very rare) has been found in the same locality.

OXICHLORIDE OF LEAD. When chloride of lead is heated in the air till it ceases to give off fumes, a compound remains $= \text{PbCl} + \text{PbO}$: it may also be formed by fusing together atomic equivalents of chloride and oxide, or chloride and carbonate of lead; it is a yellow crystalline compound. *Mendipite*, the *native oxichloride* above alluded to, appears to be $\text{PbCl}, 2\text{PbO}$. Other combinations may be formed by fusion. A hydrated compound of chloride and oxide of lead is sometimes prepared by acting upon a solution of common salt by litharge; solution of soda, and oxide and chloride of lead are formed; this insoluble residue, when rendered anhydrous by fusion, is known under the name of *patent yellow*, *Turner's yellow*, or *Cassel yellow*. When treated by nitric acid, it forms nitrate of lead, and a portion of chloride separates. A similar compound may be obtained by fusing together 1 part of chloride with 4 or 5 of oxide of lead, or by heating 1 part of sal-ammoniac with 10 of oxide of lead. According to Berzelius, a hydrated tribasic oxichloride of lead, $\text{PbCl}, 3\text{PbO}, \text{HO}$, is thrown down in the form of a white insoluble powder when ammonia is added to a solution of chloride of lead. In fusing these oxichlorides great care must be taken to avoid the presence of inflam-

mable matter, by which they are readily discolored in consequence of the reduction of a portion of lead; their fusion is best effected in a muffle.

CHLORITE OF LEAD. Millon describes a salt represented as PbO, ClO_3 . (*Ann. Ch. et Ph.*, N.S. vii. 327.)

CHLORATE OF LEAD, PbO, ClO_5 , is obtained by digesting the protoxide in chloric acid; it separates by slow evaporation, in white crystalline flakes, of a very sweet taste. When heated, it gives out oxygen, and becomes a chloride. When chlorine is passed through protoxide of lead diffused in water, chloride and peroxide of lead are formed, but no chlorate. (*VAUQUELIN, Ann. de Ch.*, xcv.) By saturating pure chloric acid with oxide of lead, and evaporating the filtered solution over a spirit lamp, Waechter obtained this salt in rhombic prisms, becoming opaque by exposure to air, $(\text{PbO}, \text{ClO}_5, \text{HO})$ soluble in water and alcohol, and detonating violently when mixed with combustibles and subjected to the blow of a hammer. At 302° they lose 4.59 per cent. of water, and at 446° suddenly decompose into chlorine, oxygen, and a black residue of peroxide and chloride of lead, which, on further ignition, becomes a definite basic compound $= \text{PbO}, 2\text{PbCl}$.

PERCHLORATE OF LEAD. PbO, ClO_7 . The solution of oxide of lead in perchloric acid yields small prisms, not deliquescent, but soluble in about their own weight of water. (*SERULLAS.*)

IODIDE OF LEAD, PbI , may be formed by heating leaf-lead with iodine; it is most readily obtained by adding iodide of potassium to solution of nitrate of lead, in equivalent proportions: it then falls in the form of a bright yellow powder, soluble in about 1250 of cold, and 200 parts of boiling water, and separates as this solution cools, in beautiful brilliant flakes, which are often hexahedral: their sp. gr. is about 6.1. In this crystalline state it retains its color, but the pulverulent iodide becomes pale by exposure to light. When gently heated it becomes deeper colored, and even brown, but again yellow on cooling: at higher temperatures it fuses, and volatilizes at a strong red-heat. When boiled in water with zinc or iron, iodides of those metals are formed and lead precipitated. It is soluble in aqueous solution of potassa and soda, forming double salts; boiled with carbonate of potassa, it forms carbonate of lead and iodide of potassium. It becomes white when digested in caustic ammonia, forming an *iodo-plumbate* $= \text{NH}_3, \text{PbI}$; the same compound is obtained by the action of gaseous ammonia upon the iodide. Iodide of lead is soluble in boiling hydrochloric acid, and the solution as it cools deposits radiated prismatic crystals of a yellow color, composed of iodide and chloride of lead. It dissolves in concentrated solutions of the alkaline iodides, but is thrown down when they are largely diluted. An *iodide of lead and sodium* is thus formed by adding slight excess of iodide of sodium to a hot solution of iodide of lead, and placing the liquid in a warm place: it separates in yellow shining laminae $= \text{NaI}, 2\text{PbI}$. It appears slightly soluble in alcohol. It consists of

						Henry.	Brandes.		
•Lead	1	...	104	...	45.22	...	45.1	...	44.98
Iodine	1	...	126	...	54.78	...	54.9	...	55.02
<hr/>									
Iodide of lead	1		230		100.00		100.0		100.00

OXIODIDES OF LEAD. According to Denot and Brandes, there are three of these compounds. (1.) PbI, PbO , formed by adding excess of acetate of lead to iodide of potassium, and boiling the precipitate in water to dissolve out the iodide of lead; or better, by precipitating iodide of potassium by bibasic acetate of lead: it is a yellow or greenish-yellow compound, fusible at a dull red-heat, insoluble in water, and resolved by acetic acid into oxide of lead, which is dissolved, and iodide, which remains. (2.) $\text{PbI}, 2\text{PbO}$ falls on adding tribasic acetate of lead to excess of iodide of potassium. (3.) $\text{PbI} + 5\text{PbO}$ is the result of the decomposition of sexbasic acetate of lead by iodide of potassium. (GRAHAM.)

A red compound of iodine and oxide of lead is formed, according to Jammes, by placing pure and moist hydrated oxide of lead in contact with recently-prepared tincture of iodine, or with powdered iodine, and washing the product with alcohol, to separate any excess of iodine; the addition of a few drops of nitrate or acetate of lead produces a blue compound. (*Journ. de Pharm.*, April, 1843.) When iodide of lead is digested in hot hydriodic acid, the solution deposits white silky crystals on cooling, which are an *hydriodate of iodide of lead*: they are decomposed by water into hydriodic acid and iodide.

IODIDE OF LEAD AND POTASSIUM. When excess of iodide of lead is digested in a concentrated solution of iodide of potassium, a solution is formed which yields on evaporation a mass of silky crystals; this compound $= 2\text{PbI}, \text{KI}$, is decomposed both by water and alcohol, which separate iodide of lead. When the alkaline iodide is used in excess, the resulting compound is $\text{PbI}, 2\text{KI}$. (BOULLAY.)

IODATE OF LEAD, PbO, IO_5 , is thrown down in the form of a white powder on adding iodate of potassa to any of the soluble salts of lead. It redissolves in excess of the acid. (PLEISCHL.)

BROMIDE OF LEAD, PbBr , is precipitated from a solution of lead by hydrobromic acid or bromide of potassium; it is white, crystalline, fusible, and concretes on cooling into a yellow mass, the sp. gr. of which is 6.63. It is sparingly soluble in cold water, and its boiling solution deposits shining acicular crystals. When first precipitated, it is decomposed by cold sulphuric and nitric acids; but when fused, it requires boiling sulphuric acid to produce that effect. (BALARD, *Ann. Ch. et Ph.*, xxxii. 359.) When heated in the air till it no longer exhales vapors, it yields a yellow *oxibromide*. It consists of

						Löwig.
Lead	1	104	57.2 59.2
Bromine	1	78	42.8 40.8
<hr/>						
Bromide of lead	1		182		100.0	100.0

BROMATE OF LEAD, PbO, BrO_5 , is thrown down in the form of a white precipitate, by adding bromic acid to a concentrated solution of nitrate of lead; it falls as a crystalline powder, $\text{PbO}, \text{BrO}_5, \text{HO}$, which becomes anhydrous when dried in vacuo over sulphuric acid. (RAMMELSBERG, *Poggend.*, lii. 96.)

FLUORIDE OF LEAD, PbF , is almost insoluble, and obtained by adding hydrofluoric acid to nitrate of lead, when it falls in the form of a white

powder, soluble in nitric and hydrochloric acids, by which, when evaporated, it is decomposed. Ammonia converts the fluoride into a *subfluoride* of lead, which is more soluble than the former. It is yellow after fusion, and easily decomposed by cold sulphuric acid. (BERZELIUS. GAY LUSAC, and THENARD.)

HYPONITRITE OF LEAD. (*Nitrite of lead. Salpetrigsaures Bleioxyd.* GMELIN. BERZELIUS.) When 1 part of neutral nitrate of lead and about 2 of metallic lead are boiled together for 12 hours in water, the filtered solution yields, on cooling, pale red acicular crystals, alkaline to tests, soluble in about 1200 parts of cold, and 34 of boiling water = $4\text{PbO}, \text{NO}_3, \text{HO}$. (CHEVREUL.) By passing carbonic acid through the solution of this salt, it loses three-fourths of its oxide, and on evaporating the filtrate in vacuo, yellow crystals, very soluble, and easily decomposed, are obtained = PbO, NO_3 . (PELIGOT.)

NITRITE OF LEAD. (*Hyponitrate of Lead. Untersalpetersaures Bleioxid.* GMELIN. BERZELIUS.) When 166 parts (1 atom) of neutral nitrate of lead, and 156 of metallic lead (1.5 atom), are boiled in a large proportion of water, the yellow filtrate yields, on cooling, orange-colored prismatic crystals, soluble in 1250 of cold, and 34 of boiling water = $7\text{PbO}, 2\text{NO}_4, 3\text{HO}$, or perhaps = $4\text{PbO}, \text{NO}_4, 2\text{HO}$. When 100 parts of neutral nitrate of lead and 63 of lead (1 atom and 1) are digested together in water at about 160° , the solution on cooling deposits yellow crystals, acid to litmus, soluble in 80 parts of water at 77° = $2\text{PbO}, \text{NO}_4, \text{HO}$. In their formation, $\text{PbO}, \text{NO}_5, + \text{Pb} = 2\text{PbO}, \text{NO}_4$. (PELIGOT, *Ann. Ch. et Ph.*, LXXVII. 87.)

NITRATE OF LEAD, PbO, NO_5 , is obtained by dissolving the metal (or better, litharge) not in excess, in hot nitric acid diluted with 2 parts of water, and evaporation. It crystallizes in tetrahedra and octohedra, which have a specific gravity = 4; they are white, anhydrous, translucent, harder than alum, and of a styptic taste; they decrepitate when heated, and when distilled give out nitrous acid vapor and oxygen, and protoxide of lead remains in the retort; they are soluble in between 7 and 8 parts of water at 60° , producing cold; they are insoluble in alcohol, and in nitric acid. This salt is of much use in analytical chemistry as a test of the presence of free and combined sulphuric acid (except in *alkaline* solutions, which should be first neutralized with nitric acid): the precipitate (which is *sulphate of lead*) is almost insoluble in nitric acid. Carbonic acid, and the alkaline carbonates, phosphates, oxalates, and tartrates, form precipitates in a solution of nitrate of lead, but the precipitates are soluble in nitric acid. The iodides and bromides, and the chlorides, when not very dilute, also precipitate the solution of nitrate of lead: all these precipitates are *white*, with the exception of those by the soluble iodides, which are *yellow*. With sulphuretted hydrogen this solution of lead forms a dark brown or black precipitate of sulphuret of lead. Nitrate of lead is always anhydrous, and consists of

						Döbereiner.	Chevreul.
Oxide of lead	1	...	112	...	67.47	...	67
Nitric acid	1	...	54	...	32.53	...	33
<hr/>							
Nitrate of lead	1		166		100.00		100

DINITRATE OF LEAD. BIBASIC NITRATE OF LEAD, $2\text{PbO},\text{NO}_5$, may be formed by boiling a mixture of equal weights of nitrate and protoxide of lead in water, filtering while hot, and setting by to crystallize ; it forms pearly crystals, of a sweet astringent taste, scarcely soluble in cold water, but much more soluble in boiling water. (CHEVREUL, *Ann. de Ch.*, LXXXII.) The presence of this salt is said to give a yellow tint to the crystals of the neutral nitrate, sometimes erroneously referred to iron: it consists of

						Chevreul.	Berzelius.
Oxide of lead	2	224	89.58 80.14
Nitric acid	1	54	19.42 19.86
<hr/>						<hr/>	<hr/>
Dinitrate of lead		1		278		100.00	100.0

When a mixture of carbonate and nitrate of lead and water is heated, carbonic acid is copiously disengaged, and on filtering the boiling solution it deposits crystals, $2\text{PbO},\text{NO}_5,\text{HO}$. (PELOUZE, *Ann. Ch. et Ph.*, 3 Ser., iv. 107.)

TRIBASIC, OR TRISNITRATE OF LEAD. $6\text{PbO},2\text{NO}_5,3\text{HO}$. When ammonia is added somewhat in excess to a solution of the neutral nitrate, the mixture digested in a closed flask, and further additions of solution of the nitrate so made as that ultimately the slightest excess only of ammonia may be perceptible, the precipitate, well washed and dried out of contact of air, consists of

						Berzelius.
Oxide of lead	6	672	83.27
Nitric acid	2	108	13.38
Water	3	27	3.35
<hr/>						<hr/>
Tribasic nitrate of lead	1		807		100.00
						100.00

SEXBASIC NITRATE OF LEAD, $6\text{PbO},\text{NO}_5,\text{HO}$, is an almost insoluble white powder, formed by precipitating the solution of the neutral nitrate by ammonia, washing the precipitate, and digesting it for 12 hours in solution of ammonia. (BERZELIUS.)

SULPHURET OF LEAD, PbS , may be formed artificially by fusion: when lead melts, it suddenly combines with sulphur with ignition. Its lustre and color much resemble pure lead, but it is brittle, and requires a bright red-heat for fusion. At a white-heat it sublimes. Its specific gravity is 7.58. Boiled with hydrochloric acid, chloride of lead and sulphuretted hydrogen are formed; with nitric acid it is converted into sulphate of lead; or, if the acid be dilute, nitrate of lead is formed, and sulphur separates. Sulphuret of lead may be obtained in the humid way, by precipitating any salt of lead by sulphuretted hydrogen: the precipitate is black, or brown if the solution be very dilute: this is so delicate a test of lead, that, according to Pfaff, a solution containing a hundred-thousandth part of the metal is discolored by it, provided no excess of acid be present. Sulphuret of lead consists of

								Proust.	Vauquelin.	Wenzel.	J. Davy.
Lead	1	104	86.37	86 86.23 86.8 86.9
Sulphur	1	16	13.63	14 13.77 13.2 13.1
<hr/>								<hr/>	<hr/>	<hr/>	<hr/>
Sulphuret of lead		1		120		100.00		100		100.00	100.0
											100.0

Native Sulphuret of Lead, or *Galena*, is the principal source of the commercial demands of the metal. It occurs massive and crystallized, chiefly in the older secondary rocks. Its primitive form is the cube, of which there are several modifications, and among them the octohedron. It often contains traces of silver, and sometimes in such quantity as to render it worth separating, which is effected by exposing the roasted sulphuret to the action of heat and air in shallow earthen dishes; the lead becomes oxidized and converted into litharge, while the silver is left pure, in consequence of its power of resisting the influence of heat and air. This process is called *cupellation*. The litharge is afterwards reduced by fusion with charcoal. “Whenever galena contains above 5 *per cent.* of silver, several other metals are usually associated with it: the proportion, which may be profitably extracted, is about 2 parts of silver in 1000.” (URE.) There is a specular variety of galena, called in Derbyshire *slickensides*, and when the rock pervaded by it is touched by the miner’s pick, it often splits asunder with a kind of explosion.

The reduction of *galena* upon a large scale is, in theory, a sufficiently simple process. The picked ore, after having been broken and washed, is roasted in a reverberatory fire, the temperature being such as to soften but not fuse it. During this operation, it is raked till the fumes of sulphur are dissipated, when it is brought into perfect fusion; the lead, reduced by the fuel, sinks to the bottom, and is run out into oblong moulds called *pigs*; the scorïæ are again melted, and furnish a portion of less pure metal. “A simple and beautiful process of reduction of sulphuret of lead consists in roasting the ore at a moderate temperature, so that about one-half of it shall be converted into sulphate of lead by oxidizement, without any of the sulphuric acid being driven off; and then, having mixed this up well with the unaltered portion of the ore, increasing the temperature very rapidly so that the two shall be fluxed together: the result is, the complete conversion of the mixture into sulphurous acid gas which passes off, and pure metallic lead which remains, the sulphur of the unaltered ore combining with the sulphur and oxygen of that portion which had been oxidized: $PbO,SO_3 + PbS = 2Pb, + 2SO_2$.” (KANE.) The mines of Great Britain afford an annual produce of about 32,000 tons of smelted lead, of which nearly the whole is obtained from the sulphuret. (URE’S *Dictionary*. DUMAS, iv. 249: where the processes of reduction are described in detail.)

The compounds described as *subsulphurets of lead* are probably mixtures of lead with the sulphuret.

HYPOSULPHITE OF LEAD, $PbO,S_2 O_2$, is precipitated in the form of a white powder, by adding solution of nitrate of lead to hyposulphite of potassa or lime. At 212° it becomes dark-colored, and at a higher temperature it burns like tinder. Distilled in close vessels, it gives out sulphurous acid, and is converted into sulphuret and sulphate of lead. It requires more than 3000 parts of cold water for solution. It is composed of

							Herschel.
Oxide of lead	1	112	79	70·30
Hyposulphurous acid	1	48	30	29·70
<hr/>							
Hyposulphite of lead	1		160		100		100·00

SULPHITE OF LEAD, PbO,SO_2 , may be obtained by digesting protoxide of lead in sulphurous acid ; or by adding sulphurous acid or sulphite of potassa to nitrate of lead. It is white, insoluble, and tasteless. When heated it loses sulphurous acid. It is converted by nitric acid into sulphate of lead. It disengages sulphurous acid when acted upon by hydrochloric, and by sulphuric acid. It consists of

						Thomson.	Gay Lussac.			
Oxide of lead.....	1	...	112	...	77.77	...	74.5	...	78	
Sulphurous acid	...	1	...	32	...	22.23	...	25.5	...	22
<hr/>										
Sulphite of lead	1		144		100.00		100.0		100	

HYPOSULPHATE OF LEAD, $\text{PbO},\text{S}_2\text{O}_5$, is formed by digesting carbonate of lead in hyposulphuric acid, filtering and evaporating. It forms soluble crystals, which, by the action of ammonia, may be so decomposed as to yield two *subhyposulphates*, namely, $10\text{PbO},\text{S}_2\text{O}_5,20\text{HO}$, and $2\text{PbO},\text{S}_2\text{O}_5$. The crystals of the neutral salt contain

						Heeren.	
Oxide of lead	1	...	112	...	50.91	...	51.04
Hyposulphuric acid.....	1	...	72	...	32.73	...	33.01
Water	4	...	36	...	16.36	...	15.95
<hr/>							
Crystallized hyposulphate of lead	1		220		100.00		100.00

SULPHATE OF LEAD. PbO,SO_3 . Cold sulphuric acid has no action upon metallic lead ; but when the metal is boiled in concentrated sulphuric acid, sulphurous acid is evolved, and a white sulphate of lead is formed. It is also easily produced by adding dilute sulphuric acid, or an alkaline sulphate, to a solution of nitrate of lead, when it falls in the form of a dense white powder, which the microscope shows to consist of crystalline grains ; hence the application of the soluble salts of lead, especially the nitrate and the acetate, as tests of the presence of sulphuric acid and sulphates. After having been dried at a temperature of 400° , it may be heated to redness in a platinum crucible without losing weight. Heated on charcoal by the blowpipe, it is decomposed and ultimately reduced. Heated with 1 atom of carbon it furnishes, at a white heat, carbonic and sulphurous acids and protoxide of lead ; with 2 atoms of charcoal it yields metallic lead. (BERTHIER.) Sulphate of lead is not *absolutely* insoluble in water : it is insoluble in alcohol, and nearly so in nitric acid ; concentrated hydrochloric acid decomposes it, and forms chloride of lead ; but on the addition of water sulphate of lead is reproduced. It is sparingly soluble in excess of sulphuric acid, and separates from it in small prismatic crystals. It is soluble, when recently precipitated, in the fixed alkalis, and sparingly so in their carbonates. Accordingly, if a weak solution of nitrate of lead be dropped into a solution of carbonate of soda containing sulphate of soda, there is either no immediate precipitate, or, if formed, it is redissolved on stirring the liquid. Sulphate of lead is soluble to some extent in acetate, tartrate, and citrate of ammonia : digested with nitrate of ammonia it yields nitrate of lead and sulphate of ammonia ; and with nitrate of baryta, nitrate of lead and sulphate of baryta. Its acid is expelled by the action of silica and of alumina at a red-heat, hence its decomposition when fused in earthen crucibles. Sulphate of lead consists of

						Klaproth.	Berthier.	Berzelius.	
Oxide of lead	1	...	112	...	73·68	...	73·5	...	73·615
Sulphuric acid	1	...	40	...	26·32	...	26·5	...	26·385
<hr/>									
Sulphate of lead	1		152		100·00		100·0		100·000

Native Sulphate of Lead is found in Anglesea, Scotland, and elsewhere, crystallized in rhombs isomorphous with sulphate of baryta. It is a rare mineral.

PHOSPHURET OF LEAD, PbP, may be formed by dropping phosphorus into melted lead, or by calcining phosphate of lead with charcoal. It is of the color of lead, and soon tarnishes. When struck with a hammer it becomes luminous, and sometimes takes fire. It consists, according to Pelletier, of 88 lead + 12 phosphorus: these numbers nearly correspond with

Lead	2	...	208	...	86.5
Phosphorus	1	...	32	...	13.5
<hr/>					
Phosphuret of lead	1		240		100.0

Phosphuretted hydrogen passed for two hours through a solution of acetate of lead gives a brown precipitate which yields a crystalline globule of phosphate of lead before the blow-pipe. (H. ROSE.)

HYPOPHOSPHITE OF LEAD. $\text{PbO}, \text{PO}, 2\text{HO}$. By digesting freshly precipitated carbonate of lead in aqueous hypophosphorous acid, Wurtz obtained rhombic prisms, having, when dried at 212° , the above formula: they are difficultly soluble in cold water, and precipitated by alcohol.

PHOSPHITE OF LEAD, $2\text{PbO}, \text{PO}_3, \text{HO}$, was prepared by Berzelius by mixing chloride of lead with phosphite of ammonia. It is white, tasteless, and insoluble. By digesting this salt in aqueous ammonia Rose obtained a basic salt $= 4\text{PbO}, \text{PO}_3, 2\text{HO}$.

PHOSPHATES OF LEAD. (1.) *Bibasic*, $2\text{PbO}, c\text{PO}_5$, is formed by mixing hot solutions of chloride of lead and common phosphate of soda: according to Mitscherlich, the phosphate of soda must be dropped into the solution of lead so as to leave the latter in excess, otherwise a subphosphate of lead falls. It is white; insoluble in water and in acetic acid; soluble in fixed alkaline solutions, and in nitric acid. It is decomposed by sulphuric acid, and by hot hydrochloric acid. It fuses before the blow-pipe without any reduction, and the globules crystallize in regular polyhedrons on cooling. It consists of

					Thomson.	Berzelius.	Berthier				
Oxide of lead.....	2	224	75.68	75	76	77.5
Phosphoric acid.....	1	72	24.32	25	24	22.5
<hr/>											
Bibasic phosphate of lead	1		296		100.00		100		100		100.0

(2.) *Tribasic*. $3\text{PbO}, c\text{PO}_5$. When the preceding salt is digested in ammonia, or when acetate of lead is precipitated by common phosphate of soda (acetic acid being set free) the tribasic phosphate is formed: it is less fusible than the bibasic salt, into which it passes, with the separation of metallic lead, when heated before the blow-pipe. It consists of

						Berzelius.
Oxide of lead	3	...	336	...	82.35	82.52
Phosphoric acid	1	...	72	...	17.65	17.48
<hr/>						<hr/>
Tribasic phosphate of lead	1		408		100.00	100.00

Berzelius has described an intermediate phosphate, $4\text{PbO},3\text{PO}_5$ obtained by precipitating chloride of lead by excess of monobasic phosphate of soda.

When the preceding salts are dissolved in excess of phosphoric acid the solution yields granular crystals, on evaporation, which appear to be an acid phosphate.

By precipitating a salt of lead by (bibasic) pyrophosphate of soda, Stromeyer obtained a *pyrophosphate of lead*, soluble in excess of the precipitant. A *metaphosphate* was formed by Persoz by adding ammonia to a mixture of metaphosphoric acid and nitrate of lead.

Native Phosphate of Lead. The mineral usually so called is a compound of phosphate and chloride of lead, in which 3 atoms of the tribasic phosphate are combined with 1 of chloride. $3[3\text{PbO},\text{PO}_5] + \text{PbCl}$. It has been found in the mines of Cumberland, Durham, Yorkshire, and of Wanlock Head in Scotland, and in many of the foreign mines. Its color is various shades of green, yellow, and brown. Its primitive form is a rhomboid, but it usually occurs in six-sided prisms. It is semitransparent and brittle. Baruel has described a *double phosphate of lead and lime* from the mine of Nussiere, near Beaujeu, in the department of the Rhone: he has called it *Nussierite*. (*Ann. Ch. et Ph.*, lxii. 219.)

NITROPHOSPHATE OF LEAD. A crystallized combination of phosphate and nitrate of lead is obtained by evaporating a solution of phosphate of lead in nitric acid. Water decomposes it and resolves it into its component salts. (BERZELIUS.)

SELENIURET OF LEAD. PbSe . Lead and selenium readily combine and yield a seleniuret, which has been found *native* in the Hartz and at Fahlun. It resembles galena, but is less brilliant. It consists of

						H. Rose.
Lead.....	1	...	104	...	72.22	71.81
Selenium	1	...	40	...	27.78	27.59
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Seleniuret of lead	1		144		100.00	99.40

SELENITE OF LEAD. PbO,SeO_2 . Selenious acid and the alkaline selenites occasion a white precipitate in solutions of lead, which falls in the form of a heavy powder. It is nearly as fusible as chloride of lead, and concretes on cooling into a white crystalline mass; it is almost insoluble in water, and difficultly decomposed by boiling sulphuric acid. It consists of

						Berzelius.
Oxide of lead	1	...	112	...	66.66	
Selenious acid	1	...	56	...	33.34	
<hr/>						<hr/>
Selenite of lead	1		168		100.00	

SELENIATE OF LEAD is a white insoluble powder. (MITSCHERLICH.)

CARBURET OF LEAD. The compounds described under this name are probably mixtures of finely-divided metallic lead and charcoal. They are obtained by decomposing tartrate of lead or cyanide of lead in close vessels: the former has already been mentioned as a *pyrophorus*.

CARBONATE OF LEAD. CERUSE. WHITE LEAD. PbO, CO_2 . This important compound of lead is made upon a large scale, and extensively employed as a white oil-paint, which is also the basis of the greater number of other colors: in England it is chiefly made in London and at Newcastle-on-Tyne, to the annual amount of about 16,000 tons. There are many processes by which it may be obtained, and much ingenuity has been displayed in their modification and improvement, the great objects being to obtain it in such a state as that it shall form the most opaque and densest *body*, as it is called, when ground up with linseed, or other drying oil, and shall at the same time be of a pure and perfect white.

The following is an outline of the several methods by which carbonate may be formed. 1. By the precipitation of any of the soluble salts of lead by means of the alkaline carbonates. A solution of nitrate or acetate of lead is thus decomposed by carbonate of soda; it yields a dense white precipitate, which, when washed and dried, is of a pure white, but when examined by a magnifier is found to consist of minute crystalline grains, a circumstance which interferes with its body or opacity to such an extent as to render it unfit for oil paint: it is also a pure or neutral carbonate, and it will appear that the most esteemed *white lead* generally contains more or less oxide or hydrated oxide of lead. It varies in texture according as the carbonate is added to the nitrate, or the nitrate to the carbonate; the latter mode of precipitation, with properly diluted solutions, furnishes the most impalpable powder. When the carbonate has once acquired the crystalline texture, no grinding or mechanical comminution is capable of conferring upon it the qualities which fit it for an oil pigment. 2. When carbonic acid gas is passed through a hot solution of subnitrate of lead, carbonate of lead is thrown down, and the solution reverts to the state of neutral nitrate: this is reconverted into subnitrate by boiling with protoxide of lead (powdered litharge), and the precipitation continuously repeated. This is the basis of Button and Dyer's patent process: they obtain carbonic acid for the decomposition of the subnitrate, by the combustion of coke, and the gas is purified from sulphurous acid and sulphuretted hydrogen by passing it through a washing apparatus, containing chalk and white lead diffused through water: the precipitated carbonate of lead is well washed, subjected to great pressure so as to condense it into cakes, and then dried in stoves. 3. Subacetate of lead is decomposed by passing through it a current of purified carbonic acid gas. The celebrated white lead of Clichy is thus prepared. 4. Granulated lead is agitated with water, by which a quantity of hydrated oxide of lead is formed, and this is subjected to the action of carbonic acid: this process was carried on in a large factory at Pimlico, under a patent granted to B. C. Torassa, Wood, and Co., but was soon abandoned. 5. Finely powdered litharge is moistened, mixed with a very little acetate of lead, (about a hundredth part,) and submitted during constant stirring to a current of heated carbonic acid: in this process, patented by Gossage and Benson of Birmingham, a subace-

tate of lead is successively formed and decomposed; a small quantity only of the original acetate therefore is required. 6. In *Hemming's* process for making white lead, nitrate of soda is distilled with the requisite quantity of sulphuric acid, by which nitric acid and sulphate of soda are formed. Oxide of lead is dissolved in the nitric acid, and the sulphate is converted into carbonate of soda, in the usual way, by heating with coal and chalk. A solution of the carbonate of soda is then added to the solution of nitrate of lead, and the results are carbonate of lead and nitrate of soda. Lastly, this nitrate of soda is treated as before described. 7. In the *Dutch process*, introduced into England about 1780, lead is cast into plates or bars, or into the form of stars, or circular gratings of six or eight inches in diameter, and from a quarter to half an inch in thickness: five or six of these are placed one above another in the upper part of a conical earthen vessel something like a garden-pot, in the bottom of which there is a little strong acetic acid. These pots are then arranged side by side, on the floor of an oblong brick chamber, and are imbedded in a mixture of new and spent tan (ground oak bark as used in the tan-yard). The first layer of pots is then covered with loose planks, and a second range of pots imbedded in tan is placed upon the former; and thus a stack is built up so as entirely to fill the chamber with alternate ranges of the pots containing the lead and acetic acid, surrounded by and imbedded in the tan. Several ranges of these stacks occupy each side of a covered building, each stack containing about 12,000 of the pots, and from 50 to 60 tons of lead. Soon after the stack is built up the tan gradually heats or ferments, and begins to exhale vapor, the temperature of the inner parts of the stack rising to 140° or 150° , or even higher. The acetic acid is slowly volatilized, and its vapor passing readily through the gratings or folds of lead, gradually corrodes the surface of the metal, upon which a crust of subacetate is successively formed and converted into carbonate, there being an abundant supply of carbonic acid furnished by the slow fermentative decomposition of the tanners' bark. In the course of from 4 to 6 weeks the process is completed, and now, on unpacking the stacks, the lead is found to have undergone a remarkable change: the form of the castings is retained, but they are converted, with considerable increase of bulk, into dense masses of carbonate of lead; this conversion is sometimes entire, at others it penetrates only to a certain depth, leaving a central skeleton as it were of metallic lead, the conversion being unequal in different parts of the stack, and varying in its perfection at different seasons, temperatures, and states of the atmosphere. The stacks are so managed that they are successively being built up and unpacked. The corroded and converted gratings, or cakes, are then passed through rollers, by which the carbonate of lead (white lead) is crushed and broken up, and the central core of metallic lead (blue lead), if any remain, is easily separated: the white lead is then transferred to the mills, where it is ground up into a thin paste with water, and is ultimately reduced, by the process of elutriation or successive washings and subsidencies, to the state of an impalpable powder; it is then dried in wooden bowls placed upon shelves in a highly-heated stove, and thus brought to the state of masses easily rubbed between the fingers into a fine powder, in which the microscope does not enable us to discern the slightest traces of crystalline character. If in-

tended for the use of the painter, it is next submitted to grinding with linseed oil; and it is found that a hundred-weight of this white lead is formed into a proper consistence with 8 pounds of oil, whereas precipitated white lead requires 16 pounds of oil for the same purpose; the one covering the surface so much more perfectly, and having so much more body than the other. It is sometimes supposed that in this process the oxygen and carbonic acid required to form the carbonate of oxide of lead are derived from the decomposition of the acetic acid; but this is evidently not the case, for not more than 100 pounds of real acetic acid exist in the whole quantity of the diluted acid contained in the several pots of each stack; and in 100 pounds of acetic acid there are not more than 47 to 48 pounds of carbon, whereas 6740 pounds would be required to furnish the carbonic acid which should convert 50 tons of lead (the average weight of that metal in each stack) into carbonate of lead. There can be no doubt then that the carbon or carbonic acid must come from the tan, and that the oxygen is partly derived from the same source, and partly from the atmosphere: the principal action of the acetic acid, therefore, is to form successive portions of subacetate of lead, which are successively decomposed by the carbonic acid: the action is, however, of a very remarkable description, for even masses of lead, such as blocks of an inch or more thickness, are thus gradually converted through and through into carbonate, so that if due time is allowed there is no central remnant of metallic lead. The original texture of the lead is much concerned in the extent and rapidity of the conversion. Rolled or sheet lead will not answer, and the gratings, coils, and stars which are employed, are all of cast lead. The purest metal is also required; for if it contain iron, the resulting white lead acquires a tawny hue, and if a trace of silver, it acquires a perceptible dinginess when it is subjected to the action of light.

In this notice of the manufacture of white lead, I have assumed that the article which occurs in commerce is a true anhydrous carbonate, and such it sometimes is; it has, however, been observed by Mulder, that it very commonly contains variable proportions of protoxide. According to his analyses, there are three varieties of commercial white lead, represented as follows:—

No. 1.	2 atoms of carbonate of lead	+	1 atom of hydrated protoxide of lead.
2.	5	ditto	+ 2 ditto
3.	3	ditto	+ 1 ditto

Richardson's experiments, however, as quoted by Professor Graham (*Elem. Chem.*, 591), show that the quantity of oxide in the best varieties of white lead is by no means considerable; carbonate of lead contains 16·5 of carbonic acid, and 83·5 of oxide of lead *per cent.*: Richardson's specimens gave the following results:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Carbonic acid	13·70	15·83	13·70	13·03	13·24	14·61	13·71	13·99	12·99	14·95
Protoxide of lead .	86·00	83·49	85·66	85·98	86·46	84·83	86·02	86·09	86·45	85·02
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	99·70	99·32	99·36	99·01	99·70	99·44	99·73	100·08	99·44	99·97

These specimens were all dried at a temperature of 300° before analysis. No. 1 was made by transmitting carbonic acid through sub-

acetate of lead. No. 2, Krems white. Nos. 3, 4, and 5, were made by causing small pieces of lead to be agitated in a tub into which carbonic acid was passed. Nos. 6, 7, 8, 9, and 10, were made by the tan-pit process, but each by a different manufacturer. (See also HOCHSTETTER, *Ann. Ch. et Ph.*, Feb. 1843, p. 144.)

Large quantities of sulphate of baryta are occasionally added to white lead, by which its valuable properties are proportionately deteriorated; the adulteration is easily detected by digesting the sample in dilute nitric acid, which dissolves the carbonate of lead, but leaves the sulphate of baryta; the articles known on the continent under the names of *Venice white*, *Hamburgh white*, and *Dutch white*, are avowedly mixtures of sulphate of baryta with carbonate of lead, the first of equal parts, the second 2 of the sulphate, and the third 3 of the sulphate, to 1 of the carbonate. *Clichy white*, *Krems* or *Kremnitz white*, and *Silver white*, are pure white lead. A very minute addition of indigo or of lamp-black is sometimes made to white lead to give it a slight bluish shade.

Carbonate of lead is usually in the form of a heavy white powder, insoluble in water, and very sparingly soluble in aqueous carbonic acid; its specific gravity varies from 6·4 to 6·75. It entirely dissolves with effervescence in acetic and in dilute nitric acid. It is immediately discolored and ultimately blackened by sulphuretted hydrogen, whence the necessity of the most cautious exclusion of all sources of that compound in white-lead works. When carefully heated in the contact of air, carbonate of lead loses carbonic acid, and furnishes by proper management a beautiful *minium*. The components of carbonate of lead are:—

					Berzelius.		Chevreul.		Klaproth.		Chenevix.
Oxide of lead.....	1	...	112	...	83·58	...	83·5	...	83·64	...	83
Carbonic acid.....	1	...	22	...	16·42	...	16·5	...	16·36	...	15
<hr/>											
Carbonate of lead	1		134		100·00		100·0		100·00		100

Native Carbonate of Lead is one of the most beautiful of the metallic ores; it occurs crystallized, and fibrous, the former transparent, the latter generally opaque. It is soft and brittle, and occasionally tinged green with carbonate of copper, or grey by sulphuret of lead. The octohedron is its primitive form: it also occurs prismatic and tabular. It has been found in Cumberland and Durham; and the acicular variety, of great beauty, in Cornwall.

SUBCARBONATE OF LEAD. BIBASIC CARBONATE OF LEAD. $2\text{PbO}, \text{CO}_2, \text{HO}$. When lead is long exposed to the joint action of air and water, or when bright spots are scraped upon a piece of tarnished lead, and it is then immersed in a vessel about 6 inches deep, filled with water, small crystals gradually form, which, according to Yorke and Bonsdorff, are this dicarbonate, consisting of

						Bonsdorff.
Oxide of lead	2	224	87·85 86·51
Carbonic acid	1	22	8·62 9·93
Water	1	9	3·53 3·55
<hr/>						
Dicarbonate of lead.....	1		255		100·00	100·00

SESQUIBASIC CARBONATE OF LEAD. $3\text{PbO}, 2\text{CO}_2, \text{HO}$. This, according to Hochstetter, is the formula of several varieties of white lead, and is

the precipitate which falls when acetate of lead is decomposed by carbonic acid. It has also been already stated that this is the composition assigned by Christison to the crystalline powder which collects upon metallic lead, immersed in distilled water, open to the air.

						Hochstetter.
Oxide of lead	3	...	336	...	86.38	86.30
Carbonic acid	2	...	44	...	11.31	11.35
Water	1	...	9	...	2.31	2.35
<hr/>						
Sesquibasic carbonate of lead	1		389		100.00	100.00

CYANIDE OF LEAD. PbCy , falls in the form of an insoluble white powder when cyanide of potassium is added to a solution of nitrate of lead, or when hydrocyanic acid is dropped into acetate of lead: heated to redness in a glass tube, it gives out nitrogen, and leaves a pyrophoric *carburet of lead*.

CYANATE OF LEAD. PbO, CyO , is thrown down in the form of a white crystalline precipitate when cyanate of potassa is added to acetate of lead; it is anhydrous, and consists of 77 oxide + 23 acid. (WÖHLER.)

SULPHOCYANIDE OF LEAD forms yellow opaque crystals, which are obtained by mixing concentrated solutions of sulphocyanide of potassium and acetate of lead; they are resolved by water into hydrosulphocyanic acid and a basic sulphocyanide: this basic salt may be formed by adding sulphocyanide of potassium to subacetate of lead; it is an insoluble crystalline powder of a yellowish white color. (LIEBIG.)

FERROCYANIDE OF LEAD. 2PbCfy . When nitrate of lead is decomposed by excess of ferrocyanide of potassium a white precipitate falls, which, when dried and gently heated, loses water. In what may be termed its *hydrated state*, it consists, according to Berzelius, of 1 equivalent of hydrocyanate of protoxide of iron, and 2 equivalents of hydrocyanate of protoxide of lead; and, after having been heated, of

						Berzelius.
Iron	1	...	28	...	8.9	8.81
Lead	2	...	208	...	66.3	65.91
Cyanogen	3	...	78	...	24.8	23.89
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	1		314		100.0	98.61

COBALTOCYANIDE OF LEAD. Cobaltocyanide of potassium causes a slight precipitate in solution of acetate of lead; on adding ammonia, the precipitation is complete; it forms a white granular powder.

BORATE OF LEAD. $\text{PbO}, 2\text{BO}_3$, is precipitated in the form of a white powder, when borate of soda is mixed with nitrate of lead: it fuses into a colorless glass, and probably consists of 2 atoms of boracic acid and 1 of protoxide of lead. Boracic acid and oxide of lead may be fused together in all proportions; 112 of oxide and 24 of acid give a very soft yellow glass, sp. gr. 6.4; with 48 of acid the glass is less yellow and harder; and with 72 of acid it is colorless, as hard as flint glass, and highly refractive. Faraday employed this compound in conjunction with silicate of lead to form a glass for optical purposes. (*Phil. Trans.*)

ALLOYS OF LEAD. With *potassium* lead forms a brittle and very fusible alloy; it may be obtained by fusion; and according to Serullas (*Ann. des Mines*, viii.), by exposing a mixture of 100 parts of litharge and 60 of calcined tartar to a strong heat for two hours in a covered crucible. The alloy of *sodium* is less brittle and fusible. When exposed to air, these alloys suffer decomposition in consequence of the oxidizement of the alkaline bases; and in water the lead separates and the sodium is converted into soda. (GAY LUSSAC, *Recherches Phys. Chim.*, i. 241.) The alloy of lead and *manganese* has not been examined. When lead is fused with *iron*, two alloys are obtained; that at the bottom of the crucible consisting of lead with a little iron, while the superficial portion is iron with a little lead. (MORVEAU, *Ann. de Ch.*, lvii.) With *zinc*, lead forms a hard ductile alloy, (GMELIN, *Ann. de Ch.*, ix.); but this alloy is not easily obtained, for when the fused metals are stirred together, the lead subsides, and the zinc floats, and when the ingot concretes it presents two distinct strata. With *tin*, lead forms several useful alloys which are somewhat less dense than the mean. Common *pewter* consists of about 80 parts of tin and 20 of lead. Equal parts of lead and tin constitute *plumbers' solder*. When pieces of *copper* are thrown into red-hot melted lead, they soon disappear and form an alloy of a grey color, brittle, and granular in texture; what is termed *pot-metal* is an alloy of this kind. Lead has not been combined with *nickel*. With *cobalt* the alloys are hard and brittle, except where the lead predominates. (GMELIN, *Ann. de Ch.*, xix.)

CHARACTERS OF THE SALTS OF LEAD. The *soluble salts of lead* have a sweet austere taste, and are characterized by the white precipitate produced by ferrocyanide of potassium, the black by sulphuretted hydrogen, the deep-brown by hydrosulphuret of ammonia, the yellow by iodide of potassium, and the white by phosphoric acid and the soluble phosphates, and by sulphuric acid and the soluble sulphates. The *salts insoluble in water* are dissolved by soda and potassa, or by nitric acid, when the metal is rendered manifest by sulphuretted hydrogen and other tests. When these salts are boiled with carbonate of soda, they afford carbonate of lead, which may be dissolved in acetic or dilute nitric acid, and subjected to the usual tests. Heated by the blow-pipe upon charcoal, they afford a globule of metal. Lead is precipitated from its solutions, in the metallic state, by many of the other metals. Zinc and cadmium separate metallic lead from the nitrate: iron only effects its partial decomposition when in a very dilute state. Chloride of lead is slowly but entirely reduced by zinc, cadmium, and iron, but tin produces no effect except free hydrochloric acid be present. All the difficultly-soluble salts of lead may be decomposed and reduced, by mixing them with dilute hydrochloric acid, and immersing a plate of zinc in the liquid. Zinc, cadmium, and tin, decompose the *alkaline* solutions of oxide of lead, but iron is without action upon them. The appearance of the metallic lead, in these cases, depends upon the state of the solution, which, if concentrated, yields it in dull dendritic crystals, but if dilute, in large metallic leaves. When solutions of the salts of lead are filtered through charcoal, which is sometimes done for the purpose of decoloration, part or even the whole of the oxide of lead, if it only amount to about one-

twentieth of the charcoal employed, will be abstracted by and remain combined with the charcoal. When acetate and nitrate of lead are distilled with charcoal and water, free acetic and nitric acids are obtained; so that in medico-legal and other inquiries, in which the process of decolorizing is resorted to, lead may in this way be overlooked. (CHEVALIER, *Comptes Rendus*, xix. 1279.)

The most convenient way to detect lead in water, is first to examine what separates on exposure to the air, by dissolving it in warm acetic acid, and testing the solution with sulphuretted hydrogen, iodide of potassium, or bichromate of potassa; then, if this process fail, to concentrate the water to an eighth part, and again test any insoluble matter which separates; and lastly, failing this procedure also, to evaporate the water to dryness, subject the residue along with charcoal to a red-heat, act on what remains with warm dilute nitric acid, and test the solution when filtered and neutralised with an alkali. It may admit of a question whether in the event of lead being indicated in the last way only, the very minute quantity which may then be present can prove detrimental. (CHRISTISON.)

In consequence of the use of leaden vessels, various articles are frequently more or less contaminated by oxide of lead; so also are certain liquors which have been kept in flint-glass bottles: the operations of dyeing and calico-printing are sometimes inconveniently affected from such causes. (CHEVREUL, *Ann. Ch. et Ph.*, Nov. 1844.)

§ XVII. ANTIMONY. Sb. 129.

ANTIMONY, or *Stibium*, was first made known by Basil Valentine, towards the end of the 15th century. It is found *native* in Sweden, in France, and in the Hartz; but its principal ore is the *sulphuret*, the *stibium* of the ancients, which is found massive and crystallized, and of which there are several varieties; the most common is the *radiated*, which is of a grey color, brittle, and frequently crystallized in four and six-sided prisms.

Antimony is obtained from the native sulphuret by the following process. 1. Mix 8 parts of the powdered ore with 6 of tartar and 3 of nitre, and throw the mixture by spoonfuls into a red-hot crucible; then heat the mass to redness, and a button will be found at the bottom of the crucible, which is the metal as it commonly occurs in commerce, and is nearly pure. The scoriæ upon the surface contain sulphuret of potassium and antimony. 2. Antimony may also be procured by carefully roasting the native sulphuret mixed with a little charcoal to prevent caking, so as to convert it into oxide of antimony, which oxide is then reduced to the metallic state by fusion with black flux, or with the addition of common soap; a button of antimony is thus obtained, which, however, contains traces of iron and generally of potassium, and perhaps some other metals; it is further purified by again fusing it with about one-fourth its weight of oxide of antimony; on cooling, the impurities are found in the superficial slag, and the metal underneath is extremely pure. 3. The purest antimony is obtained by reducing pure oxide or oxichloride by a mixture of charcoal and alkali; or by the rapid reduction of the potassio-tartrate of antimony.

Antimony is of a silvery or tin-white color, brittle and crystalline in its ordinary texture, so that when broken it exhibits splendid facets, and the surface of the ingot as it has cooled in the crucible often has a beautiful stellated appearance; the alchemists considered this star as a mysterious guide to the secrets of transmutation. It fuses at about 800° , or at a dull red-heat, and does not expand on congealing; it is very slowly volatile at a white-heat and in the absence of air, but in a stream of hydrogen it may be distilled. Its specific heat, as determined by Regnault, is 0.05077. Its specific gravity is 6.712. (HATCHETT, *Phil. Trans.*, 1803.) Placed upon ignited charcoal, under a current of oxygen gas, antimony burns with great brilliancy, throwing off its oxide in the form of a dense yellow smoke; and if a globule of the intensely-heated metal be thrown upon the floor, or upon a black board, it subdivides into numerous smaller globules, which burn as they roll along, and leave a series of white or yellowish lines of oxide. The equivalent of antimony is 129. (129 GMELIN: 64.62 TURNER: 129.24 GRAHAM.) Its symbol is Sb (Stibium.)

ANTIMONY AND OXYGEN. There are four oxides of antimony, namely, a suboxide, a salifiable oxide, and antimonious and antimonie acids. Adopting 129 as the equivalent of antimony = Sb, these compounds are respectively represented by SbO, SbO₃, SbO₄, and SbO₅. The salts of antimony properly so called, contain the second of these oxides, it being the only *basic oxide* of the metal, so that it is generally merely designated *oxide of antimony*. The third and fourth oxides combine with bases, forming salts distinguished as *antimonites* and *antimoniates*. The first, like other suboxides, is resolvable into oxide and metal by certain acids, but does not combine with them to form distinct salts. The number 64.5 is often adopted as the atomic equivalent of this metal, in which case the suboxide is properly represented by Sb₂O; the salifiable oxide then becomes a sesquioxide = Sb₂O₃; and the two acids are represented respectively by Sb₂O₄, and Sb₂O₅.

SUBOXIDE OF ANTIMONY. SbO. A dark-grey substance obtained when antimony is the positive electrode in an aqueous solution of sulphate of soda; or when powdered antimony is in contact with a platinum wire under the same circumstances. It is only by electrolytic action that this oxide has as yet been obtained. (BERZELIUS.) Proust regards this as a mixture of antimony and the next oxide. When acted on by hydrochloric acid a solution of the oxide is formed, and metallic antimony remains. According to Marchand an abundant formation of a suboxide of antimony ensues at the positive pole, when a voltaic current is transmitted through a solution of emetic tartar by platinum electrodes: the product, when washed with boiling water and dried, is an homogeneous black powder: it is resolved by hydrochloric acid, and by boiling with bitartrate of potassa, into soluble oxide and metal: it contains about 94 *per cent.* of metal, and is regarded by Marchand as = Sb₃O₂. (*Journ. für prakt. Chem.*, xxxiv. 381.)

OXIDE OF ANTIMONY. SbO₃. (*Protoxide of Antimony. Sesquioxide of Antimony.*) This oxide is obtained, 1. By heating up the metal to

its point of combustion, when the vapor burns with a bluish flame, and by placing the crucible in an inclined position, acicular crystals of the oxide are deposited in its upper part, forming the *flores antimonii*, and *nix stibii*, of the older chemists. 2. To 200 parts of sulphuric acid add 50 parts of finely-powdered metallic antimony, boil the mixture to dryness, and wash the dry mass, first in water, and then with a weak solution of carbonate of potassa or soda; a white powder remains, which, when thoroughly washed with hot water, is *protoxide of antimony*. 3. By digesting finely-powdered sulphuret of antimony in about four times its weight of hydrochloric acid, sulphuretted hydrogen is evolved, and a solution of chloride of antimony is formed, which may be decomposed by excess of carbonate of potassa; carbonic acid escapes, and protoxide of antimony falls, which is collected on a filter, washed, and dried at 212° ; it is then anhydrous. 4. When ammonia is added to a concentrated solution of tartrate of potassa and antimony, and heat applied to the mixture, a white powder falls, which, when washed and dried, is protoxide of antimony. 5. Dumas gives the following as an economical method of preparing this protoxide: Heat pulverized antimony in a shallow vessel exposed to air, so as to oxidize it; when the oxidation has advanced, it takes fire and becomes ignited throughout, and the protoxide passes into antimonious acid, but is mixed with metallic antimony; the whole is then transferred to a crucible in which it is heated till it fuses, when the antimonious acid is reduced to the state of protoxide by the excess of the metal, and a mass of fused protoxide and a button of metallic antimony are the results.

Protoxide of antimony is white, fusible, and volatile at a red-heat, undergoing no change in close vessels, but condensing in acicular and sometimes in octohedral crystals; after fusion it concretes into a silky crystalline mass of a grey color; if air be present, it undergoes a kind of combustion, and passes into a higher state of oxidation. It forms no definite hydrate, but it is soluble to a very small extent in water, and the solution is rendered yellow by sulphuretted hydrogen, and after boiling, or upon being acidulated by hydrochloric acid, deposits an orange-colored precipitate. The yellow color of the sulphuretted solution is destroyed by ammonia. (CAPITAINE. *Journ. der Pharm.*, xxv.) It is decomposed by sulphur and by charcoal, and when acted on by nitric acid, is converted into peroxide; if heated with chlorate of potassa, it deflagrates, and also becomes peroxidized; it is soluble in hydrochloric acid, and it forms emetic tartar when boiled in solution of bitartrate of potassa. When recently precipitated, and digested in caustic potassa, it is partly converted into a grey powder, or crystalline grains, which is a compound of the oxide and the alkali, very difficultly soluble. A similar combination may be obtained with soda and with ammonia. This is the only salifiable oxide of antimony. It occurs *native* forming the *white ore of antimony*. It consists of

					Proust.		Berzelius.		J. Davy.
Antimony	1	129	84.31	81.5	85
Oxygen	3	24	15.69	18.5	15
<hr/>									
Protoxide of antimony	1		153		100.00		100.0		100

ANTIMONIOUS ACID. DEUTOXIDE OF ANTIMONY. SbO_4 , is the result of

the above-mentioned combustion of the protoxide. It is also obtained by exposing antimonious acid to a red-heat. It is white, but assumes a yellow color when heated; its sp. gr. is 6.69; it is fixed and infusible in the fire, a little more soluble in water than the oxide, and reddens litmus; it is nearly insoluble in nitric acid and in sulphuric acid, and sparingly soluble in hydrochloric acid, from which it is precipitated on dilution; when this hydrochloric solution is carefully evaporated, the antimonious acid is sometimes obtained in nacreous acicular crystals. It readily combines with potassa by fusion, and the resulting compound (*antimonite of potassa*) dissolves in water, and furnishes, upon the addition of an acid, a white precipitate of *hydrated antimonious acid* = $\text{SbO}_4\text{H}_2\text{O}$, which, when thoroughlyedulcorated, has the property of reddening litmus. Antimonious acid consists of

					Proust.	Thenard.	Berzelius.	Thomson.
Antimony	1	129	80.12	77	80	80.127	80.84	
Oxygen	4	32	19.88	23	20	19.873	19.16	
<hr/>								
Antimonious acid	1	161	100.00	100	100	100.000	100.00	

This oxide is sometimes regarded as = $\text{SbO}_3 + \text{SbO}_5$; or, as an *antimoniate of antimony*, composed of

Oxide of antimony	1	153	47.52
Antimonic acid	1	169	52.48
Antimonious acid.....	1	322	100.00

SALTS OF THE ANTIMONIOUS ACID. ANTIMONITES. These compounds have been examined by Berzelius. (*Nicholson's Journal*, xxxv.) They are formed by double decomposition with the solution of antimonite of potassa. In these salts the oxygen in the base is to that in the acid as 1 to 4. (According to Fremy, these salts are *antimoniates*, the antimonious acid being resolved, when heated with a base, into protoxide and antimonic acid. *Ann. Ch. et Ph.*, Decr. 1844.)

ANTIMONITE OF AMMONIA. The solution of antimonious acid in ammonia deposits a white powder on exposure, which is an acid antimonite.

ANTIMONITE OF POTASSA is formed by fusing a mixture of potassa or carbonate of potassa and antimonious acid; the product is washed in cold water to remove excess of alkali; the residue is resolved by boiling water into a soluble antimonite consisting of 23 potassa + 77 antimonious acid = KO, SbO_4 , and into an insoluble biantimonite = $\text{KO}, 2\text{SbO}_4$.

ANTIMONITE OF SODA is soluble in water.

ANTIMONITE OF LIME is a white crystalline powder, of difficult solubility in water: it is formed by double affinity.

ANTIMONITE OF BARYTA. Antimonite of potassa added drop by drop to a boiling solution of chloride of barium causes a gradual deposit of silky acicular crystals, sparingly soluble in water, and permanent in the air.

ANTIMONITE OF MANGANESE is white and moderately soluble in water.

ANTIMONITE OF COBALT is a bulky lilac-colored precipitate having no appearance of crystallization; it dissolves in hot water: when dried in the air, it retains 25 *per cent.* of water.

ANTIMONITE OF COPPER is a bulky green insoluble powder.

ANTIMONITE OF LEAD is an insoluble white powder.

ANTIMONIC ACID. PEROXIDE OF ANTIMONY. SbO_5 , is procured: 1. By acting for a considerable time upon the powdered metal, by excess of hot nitric acid, and exposing the product to a heat of about 500° . 2. By dissolving antimony into nitrohydrochloric acid, evaporating to drive off the excess of acid, and then pouring water upon the residue: the antimonie acid separates in the form of an insoluble *hydrate*, $= \text{SbO}_5, \text{HO}$. When washed upon a filter, and carefully dried at about 500° , it becomes anhydrous: at a red-heat it gradually loses such proportion of its oxygen as to become antimonious acid. 3. When antimoniate of potassa is decomposed by nitric acid, nitrate of potassa and hydrated antimonie acid (SbO_5, HO ,) are the results. 4. The *diaphoretic antimony* and *Bezoar mineral* of old *Pharmacopœiæ* consisted of this oxide, generally, however, unless washed with a dilute acid, retaining potassa, and being, according to Berzelius, $\text{KO}, 2\text{SbO}_5$. The *Antimonium diaphoreticum ablutum* of the Prussian *Pharmacopœia* is prepared as follows: half a pound of crude antimony and two pounds of nitre are reduced to a fine powder, and gradually projected into a red-hot crucible. After deflagration the mass is fused and stirred occasionally for an hour; when cold it is pulverized and welledulcorated. It should be white, tasteless, difficultly soluble in acids, not volatile, nor fusible except at a very high heat.

Antimonic acid is pale yellow, tasteless, and apparently insoluble in water, but yet reddens moistened litmus paper. Its sp. gr. is 6.25. It neither fuses nor volatilizes at a bright red-heat, but gradually loses oxygen and becomes antimonious acid: when exposed to the flame of a spirit lamp urged by a blow-pipe, it passes off slowly in white fumes. It does not decompose the alkaline carbonates in the humid way, but at a red-heat it expels their carbonic acid, and combines with the base. It dissolves in the liquid caustic alkalis, and in hydrochloric acid when in the state of hydrate; but after exposure to a dull red-heat, becomes of extremely difficult solubility. Heated with 1 atom of sulphur it yields sulphurous acid and oxide of antimony; $\text{SbO}_5 + \text{S} = \text{SbO}_3 + \text{SO}_2$; but with a larger quantity of sulphur, 5.5 atoms for instance, it yields sulphuret of antimony and sulphurous acid; $2\text{SbO}_5 + 11 \text{S} = 2\text{SbS}_3 + 5\text{S}$ 2. It consists of

				Thomson.	Berzelius.	Proust.
Antimony	1	129	76.33	73.33	76.34	77
Oxygen	5	40	23.67	26.67	23.66	23
<hr/>						
Antimonic acid or } peroxide of antimony }	1	169	100.00	100.00	100.00	100

SALTS OF THE ANTIMONIC ACID. ANTIMONIATES. These salts are obtained chiefly by double decomposition; as by adding the antimoniate of potassa to the soluble salts of the other metals: they are mostly difficultly soluble or insoluble. In the neutral antimoniates the oxygen in the base is to that in the acid as 1 to 5.

ANTIMONATE OF AMMONIA is formed by digesting hydrated antimonie acid in ammonia. On evaporation a *super-antimoniate of ammonia* is obtained in the form of a white powder.

ANTIMONATE OF POTASSA is contained in the white powder obtained by igniting a mixture of 6 parts of nitre and 1 of antimony, and washing the residue with cold water. It partially dissolves in hot water, and this solution produces precipitates of insoluble antimoniates in several other metallic solutions: an antimoniate with excess of acid remains undissolved. When a mixture of potassa and protoxide of antimony is heated in the air, oxygen is absorbed, and antimoniate of potassa formed. Wackenroder has recommended a solution of antimoniate of potassa as a test for soda; he obtains it by fusing together 500 parts of *diaphoretic antimony* with 204 of carbonate of potassa at a strong red-heat for half an hour: digested in 100 parts of hot water it dissolves, leaving some antimonie acid: when cold, the filtered solution should be preserved out of contact of air. Moderately dilute solutions of potassa-salts are not affected by this solution of antimoniate of potassa, when they are free from lime and magnesia; but the salts of soda give with it crystalline precipitates of *antimoniate of soda*. (*Chem. Gaz.*, Novr. 1843 and Jan. 1844.)

ANTIMONATE OF SODA, as thrown down from soda solutions by antimoniate of potassa, is always crystalline, forming microscopic square prisms with truncated ends: it is very sparingly soluble in boiling water.

ANTIMONATE OF LIME. Solution of antimoniate of potassa dropped into chloride of calcium produces a precipitate, at first redissolved, but afterwards permanent and adhering to the glass like carbonate of lime.

ANTIMONATE OF BARYTA is a light flocculent insoluble powder, from which dilute nitric acid abstracts the baryta and leaves the acid: it is formed by adding antimoniate of potassa to chloride of barium.

ANTIMONATE OF MANGANESE is a white powder, permanent in the air and little soluble in water. When heated it gives out water and becomes grey: at a red-heat it again becomes white.

ANTIMONATE OF IRON. Antimoniate of potassa throws down a white precipitate in the protosalts of iron, which becomes yellowish when removed from the solution and dried. When heated it gives out water and reddens. Before the blow-pipe it is reduced; the antimony is volatilized, and iron obedient to the magnet remains.

ANTIMONATE OF ZINC, precipitated by antimoniate of potassa from sulphate of zinc, is a white crystalline powder, very sparingly soluble in

water: it gives out water and becomes yellow when heated: it is not reduced by the blow-pipe on charcoal.

ANTIMONIATE OF COBALT is a red crystalline precipitate, sparingly soluble in water.

ANTIMONIATE OF NICKEL is an insoluble greenish-white powder.

ANTIMONIATE OF COPPER is a bulky green insoluble precipitate. Before the blow-pipe it leaves a button of copper and antimony.

ANTIMONIATE OF LEAD is an insoluble white powder, becoming yellow when heated, and reducible before the blow-pipe into an alloy of lead and antimony.

ANTIMONY AND CHLORINE. PROTOCHLORIDE OF ANTIMONY. (*Terchloride of Antimony. Sesquichloride of Antimony.*) SbCl_3 . 1. The powdered metal takes fire when thrown into gaseous chlorine, and a compound, at first liquid, but afterwards concreting (if the antimony be in excess,) is formed. But according to H. Rose, this product is always a perchloride, and protochloride of antimony cannot be thus formed. 2. By the distillation of 3 parts of powdered metallic antimony with 8 of corrosive sublimate. $\text{Sb} + 3\text{HgCl} = \text{SbCl}_3 + 3\text{Hg}$. 3. By dissolving oxide of antimony in hydrochloric acid, and evaporating to dryness out of the contact of air. 4. By distilling sulphate of antimony with common salt; $\text{SbO}_3, 3\text{SO}_3 + 3\text{NaCl} = \text{SbCl}_3 + 3[\text{NaO}, \text{SO}_3]$. 5. By dissolving 1 part of sulphuret of antimony in 5 of hydrochloric acid, pouring off the liquor, and distilling until the volatile part concretes on cooling, when the receiver is changed, and that which afterwards passes over is pure chloride.

Protochloride of antimony is a soft solid at common temperatures, but becomes liquid by a gentle heat, and crystallizes as it cools. It is the *butter of antimony* of old writers. It deliquesces by exposure to air, and is a powerful caustic. When water is added to this chloride a mutual decomposition ensues, and hydrated oxichloride of antimony and hydrochloric acid result. It does not absorb hydrochloric gas. It slowly absorbs about 6 *per cent.* of ammonia: the compound does not deliquesce, and the ammonia is entirely expelled by a gentle heat: it forms with sal-ammoniac a crystallizable compound $= 2\text{NH}_4\text{Cl}, \text{SbCl}_3$. (JACQUELAIN, *Ann. Ch. et Ph.*, LXVI., 128.) Protochloride of antimony consists of

					II. Rose.	Göbel.	J. Davy.
Antimony	1	... 129	... 54·43	... 53·27	... 54·98	... 60·42	
Chlorine	3	... 108	... 45·57	... 46·73	... 45·02	... 39·58	
<hr/>							
Protochloride of antimony	1	237	100·00	100·00	100·00	100·00	

Protochloride of antimony is sometimes used for bronzing metals, especially gun-barrels, which are cleaned and rubbed over with it: a film of antimony is precipitated upon the iron: some sulphate of copper is generally added to the chloride of antimony. (In reference to the separation of the protochloride from the perchloride of antimony, see a paper by M. A. Levol, *Ann. Ch. et Ph.*, 3rd Ser., i. 504.)

Poggiale has described two double salts composed of chloride of antimony and chloride of ammonium, the formulæ of which are $3[\text{NH}_4\text{Cl}, \text{SbCl}_3] + 3\text{HO}$, and $2[\text{NH}_4\text{Cl}, \text{SbCl}_3] + 2\text{HO}$. These salts are transparent, colorless, and permanent in a dry atmosphere, and are decomposed by a large quantity of water. (*Comptes Rend.* and *Chem. Gaz.*, Feb. 1846.) Analogous double salts may also be formed with the chlorides of potassium and of sodium: their formulæ are $3\text{KCl}, \text{SbCl}_3$, and $3\text{NaCl}, \text{SbCl}_3$. With chloride of barium the salt is $2\text{BaCl}, \text{SbCl}_3 + 5\text{HO}$: it forms stellated acicular crystals.

PERCHLORIDE OF ANTIMONY. PENTACHLORIDE OF ANTIMONY. SbCl_5 , is formed by passing dry chlorine over heated antimony, or by exposing the protochloride to a stream of chlorine which has been dried by transmission through oil of vitriol. It is a volatile transparent liquid, which emits copious fumes when exposed to air. When heated, it becomes protochloride by the evolution of chlorine. By exposure to air it becomes a crystalline *hydrated perchloride*, which is deliquescent and soluble without decomposition in concentrated hydrochloric acid. It consists of

						H. Rose.	
Antimony	1	...	129	...	41.74	...	40.56
Chlorine	5	...	180	...	58.26	...	59.44
<hr/>							
Perchloride of antimony.....	1		309		100.00		100.00

OXICHLORIDE OF ANTIMONY. When protochloride of antimony is mixed with a large quantity of water, a precipitate falls, which was formerly used as an emetic, under the name of *Algarotti's powder*, or *Mercurius vitæ*. The same compound is formed on diluting a solution of antimony in nitrohydrochloric acid. When first thrown down it is white and curdy, but afterwards assumes a yellowish-grey color and becomes pulverulent or crystalline: it does not dissolve in water: it is fusible, and concretes on cooling into a translucent crystalline mass. By continued washing with hot water, and by the action of the alkaline carbonates, it leaves protoxide. From the experiments of Johnston, (*N. Edinb. Phil. Journ.*, xviii. 40,) Phillips, (*Phil. Mag. and Ann.*, viii. 406,) and Malaguti, (*Ann. Ch. et Ph.*, lix. 220,) this compound appears to consist of

Antimony.....	6....774....77.24	} = {	Protochloride of an- timony	} 1....237....23.65
Chlorine	3....108....10.78			
Oxygen	15....120....11.98			
<hr/>				
Oxichloride of antimony	1 1002 100.00			1 1002 100.00

CHLORATE AND PERCHLORATE OF ANTIMONY have not been examined.

IODIDE OF ANTIMONY. SbI_3 . Antimony and iodine combine when triturated together (sometimes with explosion,) and form a brown crystalline compound, fusible and volatile without decomposition; acted upon by water, it produces hydriodic acid and an oxiodide of antimony. When powdered antimony and iodine are boiled together in water, hydriodic acid and protoxide of antimony are the results.

Iodate and Periodate of Antimony are unknown.

BROMIDE OF ANTIMONY. SbBr_3 . The action of bromine on antimony is attended by the disengagement of heat and light, and the compound is readily obtained by distillation, as in the process for preparing bromide of arsenic: it is solid at common temperatures, fusible at 206° , and boils at 518° . It is colorless, and crystallizes in needles; it attracts moisture from the air, and is decomposed by water. (SERULLAS, *Ann. Ch. et Ph.*, xxxviii. 322.)

Bromate of Antimony has not been examined.

FLUORIDE OF ANTIMONY, SbF_3 , is a white solid compound, more volatile than sulphuric acid. (DUMAS, *Ann. Ch. et Ph.*, xxxi. 435.)

ANTIMONY AND HYDROGEN. When antimony is made the negative electrode in water, a dark-brown substance (hydruret?) is slowly formed. *Antimoniuretted hydrogen gas*, SbH_3 , is formed by the action of dilute sulphuric or hydrochloric acid on alloys of zinc and antimony; or by dissolving zinc mixed with oxide of antimony in those acids. (THOMPSON, *Phil. Mag.*, x. 353.) This gas may be obtained pure by the action of dilute sulphuric acid on an alloy of equal weights of zinc and antimony; or by dissolving zinc in a solution of emetic tartar in hydrochloric acid. The gas is colorless, nearly inodorous (if free from arsenic), and is decomposed when passed through a tube heated to dull redness, depositing a brilliant coat of antimony. When burned in the air, it deposits oxide of antimony, and if the flame be in contact of glass or porcelain, metallic spots are formed resembling those produced by a similar combustion of arseniuretted hydrogen (which see.)

When antimoniuretted hydrogen gas stands for some days over water it deposits films of antimony: it is slowly decomposed by gaseous chlorine, but more rapidly when transmitted through aqueous solution of chlorine. It appears to consist of

							Lassaigne.
Antimony	1	129	97.73	97.58
Hydrogen	3	3	2.27	2.42
<hr/>							<hr/>
Antimoniuretted hydrogen gas	1		132		100.00		100.00

When a concentrated solution of sal-ammoniac is decomposed by a powerful voltaic battery, the negative electrode of which is a bar of antimony, faint detonations are heard arising from the formation of a spontaneously inflammable modification of antimoniuretted hydrogen. (MARCHAND, *Journ. fur prakt. Chem.*, xxxiv. 381.)

NITRATE OF ANTIMONY. Nitric acid acts powerfully on metallic antimony, and, if mixed with it in fine powder, will sometimes cause its inflammation: the metal becomes peroxidized, and scarcely an appreciable portion is retained in solution. As in some analogous cases of the decomposition of nitric acid, ammonia is produced, which may be rendered sensible by pouring potassa on the white magma that results, and by which the nitrate of ammonia is decomposed. Protoxide of

antimony, digested in dilute nitric acid, produces a difficultly-soluble salt, which separates in white scaly crystals, and which appears to be a *nitrate of antimony*. Neither antimonious nor antimonie acids are soluble in nitric acid.

NITROHYDROCHLORIC ACID readily dissolves antimony, and forms an orange-colored solution, which is decomposed by the addition of water. It is frequently sold under the name of *muriate of antimony*. Iron or zinc immersed into this solution throw down a black powder, which, according to Thenard, is pyrophoric.

SULPHURET OF ANTIMONY. PROTOSULPHURET OF ANTIMONY. (*Tersulphuret or Sesquisulphuret of Antimony*.) SbS_3 . This compound may be formed artificially by fusing the metal with sulphur, or by heating any of the oxides of antimony with excess of sulphur. Its color is dark-grey and metallic; its specific gravity 4.66: it closely resembles the *native sulphuret*. When this sulphuret is exposed under a muffle to a dull red-heat, it gradually loses sulphur, and absorbs oxygen, being converted into a grey powder, which consists of a mixture of protoxide of antimony and sulphuret. If the heat be increased, this fuses into a transparent substance of a yellow or brown color, formerly called *Glass of antimony*, the composition of which is variable; it generally contains about 85 *per cent.* of protoxide and 15 of sulphuret. In that which is imported for pharmaceutical purposes from Germany and Holland, there is usually a portion of silica, and it is sometimes adulterated with oxide of lead. This fraud is detected by digesting the finely-powdered glass in hot nitric acid, diluting the solution, and filtering. The filtered liquor gives a white precipitate on the addition of sulphate of soda, if lead be present. During the formation of glass of antimony, if the heat be raised too high, the greater part of the oxide sublimes in slender crystalline needles, (which are generally regarded as protoxide, but which Phillips found insoluble in a solution of bitartrate of potassa;) while another portion, if air be not excluded, passes into the state of deutoxide, and undergoes no further change at a very high temperature. Compounds of the protoxide with larger quantities of the sulphuret have been termed *Saffron of antimony* or *Crocus metallorum*, and *Liver of antimony*.

When sulphuret of antimony is deflagrated with nitre, the residue consists of sulphate and antimoniate of potassa. When boiled with sulphuric acid, sulphur is separated, sulphurous acid evolved, and a sulphate of antimony is formed, from which water precipitates a subsulphate. With hydrochloric acid, sulphuretted hydrogen is evolved, and a solution of chloride of antimony in hydrochloric acid is formed, together with more or less of the sulphuretted oxide. Chlorine passed over heated sulphuret of antimony forms chloride of sulphur and chloride of antimony. With nitrohydrochloric acid it yields chloride of antimony and sulphur, and if there be excess of nitric acid, sulphate and peroxide of antimony are also produced. Hydrogen gas passed over this sulphuret at a red-heat, carries off the sulphur in the form of sulphuretted hydrogen, and metallic antimony remains. Charcoal decomposes sulphuret of antimony at high temperatures, and sulphuret of carbon and metallic

antimony are the results: it is also desulphurized at high temperatures by the action of iron and some other metals. This sulphuret of antimony, whether native or artificial, consists of

		Berzelius. Bergman. J. Davy. Vauquelin.						
Antimony	1	129	72.88	72.8	74	74.16	75	
Sulphur	3	48	27.12	27.2	26	25.84	25	
<hr/>		<hr/>						
Sulphuret of antimony	1	177	100.00	100.0	100	100.00	100	

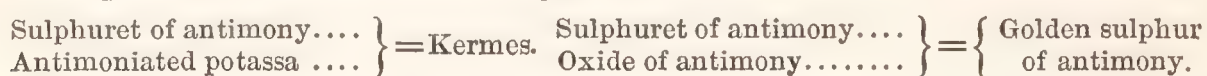
KERMES MINERAL. GOLDEN SULPHURET OF ANTIMONY. Under these names, and also under those of *Precipitated sulphuret of antimony* and *Oxisulphuret of antimony*, certain products have been described of variable composition, and respecting the nature of which chemists are not agreed.

When solutions of antimony are decomposed by sulphuretted hydrogen, red, brown, or orange-colored precipitates result, which vary in appearance and composition with the nature of the *solution*. The most definite combination of this kind is that which is thrown down when sulphuretted hydrogen is passed through an aqueous solution of the tartrate of antimony and potassa (emetic tartar). It is of a red color inclining to orange, and when dried in the air retains its color: it was generally considered as a compound of sulphuretted hydrogen and oxide of antimony (hydrosulphate of antimony); and, inasmuch as when heated it loses water and passes into the state of grey sulphuret of antimony, it was presumed that, under such circumstances, there was a mutual decomposition of the oxide and the sulphuretted hydrogen. But it has been found that this precipitate may be rendered anhydrous by careful drying, and that it still retains its red color; but that when more strongly heated it shrinks in bulk and suddenly assumes the color and lustre of the grey sulphuret: hence it has been regarded as a hydrated sulphuret of antimony, and its color (and medicinal activity?) have been referred to its state of division.

Kermes mineral is generally prepared as follows: Equal parts of sulphuret of antimony and of caustic potassa are fused together; the resulting mass is finely powdered, and boiled in ten times its weight of water. The liquor is filtered while hot; and, during cooling, it deposits *kermes*. The mother-liquor of *kermes* deposits a copious yellowish-red precipitate upon the addition of dilute sulphuric acid, which, when washed and dried, is known under the name of *Golden sulphur of antimony*.

According to Berzelius, when 3 atoms of potassa and 1 of sulphuret of antimony are fused together, they yield 3 atoms of sulphuret of potassium and 1 of oxide of antimony. $3\text{KO} + \text{SbS}_3 = 3\text{KS} + \text{SbO}_3$. The sulphuret of potassium unites with undecomposed sulphuret of antimony, forming a double sulphuret or sulphur salt; and the oxide of antimony unites with the undecomposed potassa, so that when hot water is added, a solution is obtained, holding the double sulphuret of antimony and potassium, and the compound of oxide of antimony and potassa. As the solution cools sulphuret of antimony subsides, merely because the solvent power of the sulphuret of potassium is diminished by cooling, and it carries down with it a variable quantity of antimoniated potassa, apparently in combination, inasmuch as it cannot be removed by washing. The cold solution still contains double sulphuret of antimony and potas-

sium, and also antimoniated potassa: on adding to it the dilute acid the sulphuret of potassium becomes converted into sulphuretted hydrogen and potassa (by decomposition of water), and the antimoniated potassa is decomposed by the abstraction of its potassa; so that the sulphuret and the oxide of antimony being both deprived of the principles which gave them solubility, are precipitated in the form of what is called *golden sulphuret*, and which differs from kermes in the absence of potassa and in containing more oxide of antimony, and perhaps, as Dr. Turner observes, in being or containing, an oxisulphuret. The following, therefore, are the components of kermes and the golden sulphuret, the relative proportions of their proximate elements being probably indefinite:



The *oxisulphuret of antimony* of the Pharmacopœia is probably a mixture of kermes and of the golden sulphuret; it is necessarily somewhat indefinite in its composition, and therefore objectionable as a medicine: the medical powers of the sulphuret precipitated by sulphuretted hydrogen from a solution of emetic tartar have not been well ascertained, but it would be an advantage if some definite oxisulphuret of antimony could be substituted for the above: it is certainly not very probable that a highly active antimonial, medicinally, should be a mere sulphuret of antimony, owing its activity to its state of mechanical division; whether kermes is a mixture or a combination of sulphuret of antimony with antimoniated potassa has not been determined, but it is probable that either oxide of antimony or its compound with potassa are essential to its medicinal powers; and therefore, any mere sulphuret of antimony ought not to bear the name of kermes. Phillips gives the following as the composition of the “*Antimonii oxysulphuretum*” of the Pharmacopœia. (*Trans. Lond. Pharm.*)

Sesquioxide of antimony	12·0
Sesquisulphuret of antimony	76·5
Water	11·5
	<hr/>
	100·0

Native Sulphuret of Antimony is by far the most frequently occurring ore of antimony. It occurs in prismatic and acicular crystals in the mines of Hungary and the Hartz; in France; in Cornwall; and in the Island of Borneo, whence it is brought by way of Singapore as ballast, to the annual amount of between 6 and 700 tons. This ore was known to the ancients and used by the Asiatic and Greek ladies as a pigment for the eyelashes: it was called *stimmi* (στίμμι) and *stibium* (στίβι). It used formerly to be separated from its siliceous gangue, by heating it in melting-pots, at the bottom of which were several holes through which it ran into a pot beneath; but the loss attendant upon this method has led to fusing it in a reverberating furnace from which it flows into vessels placed for its reception. It is known in commerce as *crude antimony*, and is usually met with in somewhat conical masses or loaves, presenting when broken a dark grey and striated or crystalline fracture, and metallic lustre: its powder is nearly black, and its melting-point somewhat above that of the pure metal: it is seldom pure, frequently containing the sulphurets of lead, iron, copper, and arsenic. When pure,

it is completely soluble when boiled in fine powder in hydrochloric acid; if it contain sulphuret of arsenic this remains undissolved. On largely diluting the hydrochloric solution with water, the greater part of the antimony is precipitated, and the lead, iron, and copper may then be detected by their appropriate tests.

PERSULPHURET OF ANTIMONY. PENTASULPHURET OF ANTIMONY.

SbS_5 . This compound may be formed by passing sulphuretted hydrogen through antimonious acid diffused in water, or through pentachloride of antimony dissolved in aqueous tartaric acid. It may also be obtained by dissolving, as in the preparation of kermes, an alkaline sulphuret and sulphuret of antimony, with excess of sulphur, so that the tersulphuret may be converted into pentasulphuret, and then adding an acid; $3[\text{NaS}, \text{SbS}_5] + 3[\text{SO}_3 \text{HO}] = 3[\text{NaO}, \text{SO}_3] + 3\text{HS} + \text{SbS}_5$. This pentasulphuret is an orange-colored powder, which, when heated out of contact of air, loses 2 atoms of sulphur; it dissolves in warm aqueous ammonia and in potassa and soda, and combines with the basic sulphurets. It consists of

Antimony.....	1	...	129	...	61.72
Sulphur	5	...	80	...	38.28
<hr/>					
Pentasulphuret of antimony	1		209		100.00

OXISULPHURET OF ANTIMONY. It has already been stated that *glass of antimony* is a compound of sulphuret and oxide of antimony, and that some other medicinal preparations of antimony, are also combinations of variable proportions of the sulphuret and oxide. To this class of compounds belongs also the beautiful and rare *ore* of antimony, called *red antimony*; it generally occurs in delicate capillary crystals, consisting, according to H. Rose, of 2 atoms of sulphuret and 1 of oxide of antimony.

CHLOROSULPHURET OF ANTIMONY. When chlorine is passed over tersulphuret of antimony gently heated it forms at first a brown liquid, which afterwards by absorbing more chlorine, produces a white powder, being, according to H. Rose, $\text{SbCl}_5, 3\text{SbCl}_2$.

IODOSULPHURET OF ANTIMONY is procured, according to Henry and Garot, by triturating together equal parts of iodine and sulphuret of antimony; it is of a reddish-brown color, and when heated gives a red vapor, which condenses in red laminae. It consists of 23.2 antimony, 67.9 iodine, 8.9 sulphur. This compound is very fusible and volatile, and is decomposed at a high temperature. Acted on by water it yields protoxide of antimony, sulphur, and hydriodic acid: its taste is acrid and disagreeable.

SULPHITE OF ANTIMONY is an insoluble white salt, obtained by digesting the oxide in aqueous sulphurous acid, or by passing sulphurous acid gas through a solution of oxide of antimony in hydrochloric acid.

SULPHATES OF ANTIMONY. The white saline mass formed by boiling powdered antimony in sulphuric acid, is resolved by water into an insoluble *subsulphate* and a soluble *supersulphate*: the latter may be obtained

in small deliquescent acicular crystals by evaporation. The original white salt is a tersulphate $= \text{SbO}_3, 3\text{SO}_3$; the subsulphate is $2\text{SbO}_3, \text{SO}_3$; and when the tersulphate is shaken with alcohol a white powder is obtained $= \text{SbO}_3, \text{SO}_3$. (BRANDES.)

SELENIURET OF ANTIMONY. Selenium and antimony readily combine with evolution of heat; the compound has a metallic lustre and crystalline fracture: it combines, by fusion, with the oxide, forming an *oxiseleniuret*.

PHOSPHURET OF ANTIMONY is formed by heating together equal parts of oxide of antimony and phosphoric acid, with a little charcoal. It is white and brittle. It is also formed by projecting phosphorus upon melted antimony. (PELLETIER.)

Nothing is known respecting either the *Hypophosphite* or the *Phosphite* of antimony.

PHOSPHATE OF ANTIMONY. When oxide of antimony is digested in phosphoric acid it is dissolved, but affords no crystallizable salt on evaporation. (WENZEL.) The acid solution yields, according to Brandes, small prismatic crystals $= 2\text{SbO}_3, 3\text{PO}_5, 2\text{HO}$, which after washing with cold water leave a salt $= 2\text{SbO}_3, \text{PO}_5$; and this, after long edulcoration with boiling water, becomes $4\text{SbO}_3, \text{PO}_5$.

ANTIMONIAL POWDER. In the *London Pharmacopœia* there is a preparation called *Pulvis Antimonii Compositus*, formed by heating 1 part of sulphuret of antimony with 2 of hartshorn-shavings. The action of heat upon the sulphuret has already been described. Its effect upon the hartshorn-shavings is to destroy the animal matter, leaving little else than phosphate of lime: so that the *Pulvis Antimonialis* consists essentially of an oxide of antimony, mixed with phosphate of lime. This preparation is usually considered analogous to, if not identical with, *James's Powder*, which, according to Dr. Pearson's analysis (*Phil. Trans.*, 1791), consists of 43 phosphate of lime, and 57 oxide of antimony. Be this as it may, the antimonial powder of the *Pharmacopœia* is an uncertain and ill-contrived preparation: its activity depends upon the proportion of protoxide which it contains; but a great part of the protoxide may be volatilized, or converted into deutoxide, of a mixture of which, with phosphate of lime, the antimonial powder generally consists. Accordingly, in examining antimonial powder from various sources, prepared after the direction of the *Pharmacopœia*, it is found of variable composition; and it is very difficult so to conduct the process as to obtain, upon the large scale, an uniform product. For medical use, *emetic tartar* seems the only certain and necessary preparation of antimony; if, however, a compound of the nature of the antimonial powder be requisite, one of the best modes of preparing it would be to dissolve certain proportions of protoxide of antimony and phosphate of lime in hydrochloric acid, precipitate by ammonia, and edulcorate with water. Mr. Chenevix advises for this purpose equal parts of the oxide and phosphate, but such proportion of antimony is too great. (See in reference to the composition and properties of James's powder and antimonial powder, PEREIRA, *Mat. Med.*, 404.)

Neither *Carbonate*, *Cyanide*, nor *Borate* of antimony are known to exist.

ALLOYS OF ANTIMONY. With *potassium* and *sodium* antimony forms white brittle compounds, destructible by the action of air and water. The *alloy of potassium and antimony* may be formed by heating to redness in a covered crucible a mixture of equal parts of finely-powdered antimony and tartar for about three hours. When cold, the crucible must be broken, the button of alloy freed from the scoriæ, broken into pieces, and preserved in a well-stopped phial. By substituting tartrate of soda for common tartar the *alloy of sodium and antimony* may be obtained: and a mixture of soda-tartrate of potassa and powdered antimony, yields the *triple alloy of antimony, potassium, and sodium*. When these alloys are reduced to powder, and exposed to air, they heat, and take fire like pyrophorus, and if blended with excess of carbon they burst into sudden ignition on exposure, and especially on the addition of a few drops of water. (SERULLAS, *Ann. des Mines*, vi.) Nothing is known of the alloys of antimony with the other light metals, nor with *manganese*, *cadmium*, or *cobalt*. Antimony and *iron* combine by fusion, and form a white alloy, the density of which exceeds the mean of its components. 2 parts of sulphuret of antimony fused with 1 of iron, yield a slag of sulphuret of iron, and an alloy which was formerly called *Martial regulus*. The magnetic quality of iron is said to be more diminished by antimony than by any other metal. *Zinc* and antimony form a hard brittle alloy of the color of steel, the density of which is below the mean: it is very combustible. (GELLERT.) Antimony and *tin* may be fused together in various proportions: an alloy of 1 atom of each is brittle and pulverizable: its specific gravity is 6.803. (CHAUDET.) 1 part of antimony and 10 of tin form a ductile compound, which a little lead renders brittle. A fine pewter is said to consist of 12 parts of tin and 1 of antimony, with a small addition of copper. (*On the quantitative separation of antimony and tin*, see LEVOL and ELSNER, *Chem. Gaz.*, March, 1846.) When 1 part of *nickel* and 2 of antimony are fused together, they form a dark-grey compound. (GEHLEN.) *Copper* combines with antimony by fusion, and when the alloy contains equal weights of the two metals, it is of a violet color. (GELLERT.) An alloy of 1 of antimony and 3 of copper is lamellar and brittle, but takes a good polish. When there is excess of antimony the alloy is white. *Lead* and antimony form an important alloy: when the metals are in equal weights, the compound is brittle: 3 of lead and 1 of antimony form a compact hard alloy: 12 of lead and 1 of antimony give a very malleable alloy, harder than lead. *Type metal* is a compound of 4 parts of lead and 1 of antimony; its hardness is such as to resist the pressure to which in the printing-press the type is necessarily subjected: it is readily fusible, and takes a very sharp impression from the matrix or mould in which the letter or stereotype plate is cast. A good *white metal*, used for spoons and tea-pots, and sometimes called *Britannia metal*, is composed of 100 tin, 8 antimony, 2 bismuth, and 2 copper.

CHARACTERS OF THE SALTS OF ANTIMONY. The salts of the oxide of antimony, when dissolved in water, or in an acid, are decomposed by the

immersion of a plate of zinc, and the metal is thrown down in the form of a black powder, which, when dried in the air, and then gently heated, is often pyrophoric. Iron, tin, lead, cadmium, and cobalt, act nearly as zinc, but with copper the precipitation of metallic antimony is imperfect. Sulphuretted hydrogen produces a distinctive brownish-red or dark orange precipitate in salts of antimony with excess of acid, but if they be neutral, their color is only changed, and the precipitate does not ensue till acid is added. The alkaline hydrosulphurets produce a similar precipitate, which is in almost all cases redissolved by excess of the precipitant, especially when aided by heat. Many of the saline combinations of antimony are decomposed when largely diluted with water, and a basic salt is thrown down: this decomposition is generally prevented by the presence of excess of tartaric acid. Ammonia throws down the oxide of antimony, especially when aided by heat, in the form of a white flocculent precipitate, insoluble in excess of ammonia. Potassa also throws down the oxide, but is apt, if in slight excess, to combine with it and form granular crystals, which adhere to the sides of the test-glass. Ferrocyanide of potassium gives a white precipitate, insoluble in hydrochloric acid, and ferridcyanide no precipitate in the salts of antimony. Such of these salts as are insoluble in water, are soluble in hydrochloric acid, and the metal is then recognised by the same tests.

Before the blow-pipe, oxide of antimony is partly reduced in the exterior flame, and spreads a white smoke on the charcoal. In the interior flame it is readily reduced. With microcosmic salt and with borax it forms a hyacinth-colored glass. Metallic antimony, when ignited on charcoal, becomes covered with acicular crystals of oxide. Sulphuret of antimony fuses upon charcoal, and is absorbed.

§ XVIII. BISMUTH. Bi. 213.

THIS metal was first described by Agricola, in 1529. It was sometimes called *Marcasite*. It is found *native*, and combined with oxygen, and with arsenic and sulphur. It is neither of common occurrence nor very abundant. *Native Bismuth* occurs crystallized in octohedra and cubes, and generally contains arsenic, and sometimes cobalt. It has been found in Cornwall, and in Germany, France, and Sweden.

Bismuth is a brittle white metal with a slight tint of red: its specific gravity is 9.822. (HATCHETT, *Phil. Trans.*, 1803.) 9.799, at 68°, when perfectly pure. (MARCHAND.) When its specific gravity exceeds 9.83, it is probably impure. The specific heat of bismuth is 0.03084. It fuses at 476° (CRICHTON), 507° (RUDBERG), and always crystallizes on cooling. According to Chaudet, pure bismuth is somewhat flexible. A cast bar of the metal, $\frac{1}{10}$ of an inch diameter, supports, according to Muschenbroeck, a weight of forty-eight pounds. Bismuth is volatile at a high heat, and may be distilled in close vessels. It transmits heat more slowly than most other metals, perhaps in consequence of its texture, which is highly crystalline. (Fig. 12, p. 8.) To obtain good crystals, the bismuth requires to be purified by fusion with nitre, by which sulphur and arsenic, usually present in the metal as it occurs in commerce, are separated. When thus refined the metal is carefully melted, and poured into a heated mould;

such as a common ingot, or a brass or iron mortar, where it is suffered slowly and quietly to cool. When the surface has solidified, the crust is pierced, and the liquid metal poured out from the interior: the mould is then suffered to cool, and the superior crust carefully removed, when the cavity is found lined with beautiful cubical crystals, usually highly iridescent. Bismuth is placed by Faraday at the head of the diamagnetic substances. (See *note*, p. 258.) It boils at a white-heat, and sublimes; and, according to Regnault, at this high temperature, it decomposes the vapor of water; but not, according to Berzelius.

Arsenic, iron, copper, nickel, silver, and other metals, are frequently found in the bismuth of commerce: if arsenic be present, it is recognised by the odor of its vapor under the blow-pipe, or by fusion with 2 parts of zinc and testing in Marsh's apparatus. (See ARSENIC.) To purify bismuth it may be dissolved in nitric acid, and the clear solution poured off into water, which occasions a copious precipitation of a nitrate of bismuth, easily reducible by fusion with charcoal or black flux, in an earthen crucible.

BISMUTH AND OXYGEN. There are three oxides of bismuth, but only one which is salifiable, and of this the atomic constitution has been variously represented: some, grouping it with the magnesian family of oxides, view it as BiO , and assume 71 as the atomic weight of bismuth; others have regarded it as Bi_2O_3 ; and others, upon the strength of the analogies between antimony and bismuth, as BiO_3 ; in the latter case the equivalent of bismuth becomes 213, which I have adopted. (213, GMELIN: 213.3, KANE: 106.5, BERZELIUS: 71.07, GRAHAM: TURNER.)

SUBOXIDE OF BISMUTH. The existence of a distinct suboxide of bismuth is admitted by Berzelius and Vogel, but doubted by Proust and Davy. It is said to be formed by the action of air on bismuth heated a little above its melting-point, when a grey powder gradually collects upon it, and also to be deposited upon the negative electrode, when a very feeble electric current is transmitted through a nitric solution of bismuth. According to Vogel it is formed by digesting basic nitrate of bismuth in a close vessel, with excess of protochloride of tin: it forms a black powder, which, when washed and dried in vacuo, is so inflammable as to burn like tinder into oxide, and is soluble in hot hydrochloric acid: by dilute nitric acid it is resolved into oxide, which is dissolved, and into metallic bismuth, which remains as a grey powder.

OXIDE OF BISMUTH. PROTOXIDE OF BISMUTH. BiO_3 . When bismuth is exposed to a white-heat, or when a current of oxygen is directed upon the heated metal, it burns, and produces an abundant yellow smoke, which condenses in the form of a yellowish-white sublimate. The readiest mode of obtaining this oxide consists in dissolving bismuth in nitric acid, precipitating by dilution with water, edulcorating the precipitate, and heating it, when dry, nearly to redness. At a red-heat this oxide fuses into a brown liquid, and when in fusion it acts upon other oxides much in the same way as oxide of lead; it also acts upon earthen crucibles. It forms, on cooling, a yellow vitreous mass of a specific gravity of 8.2. It is easily reduced by hydrogen, charcoal, and several of the metals. It is decomposed by chlorine, but not by iodine. It combines with water into a

white pulverulent *hydrate*, which is best obtained by digesting the precipitate formed by pouring the nitric solution of bismuth into water, in caustic potassa or soda, and washing and drying at 80° : it is insoluble in excess of the alkalis (and their carbonates); and when boiled with them becomes yellow and anhydrous. This oxide consists of

						Lagerhielm.	L. Gmelin.	J. Davy			
Bismuth	1	213	89.87	89.86	89.67	90
Oxygen.....	3	24	10.13	10.14	10.33	10
<hr/>											
Oxide of bismuth	1		237		100.00		100.00		100.00		100

Native Oxide of Bismuth is a very rare mineral; it has been found in Cornwall and Saxony: it is the *Bismuth Ochre* of some mineralogists.

PEROXIDE OF BISMUTH. BISMUTHIC ACID. BiO_5 . This oxide was first noticed by Bucholz and Brandes; it was afterwards examined by A. Stromeyer. It is formed when hydrate of potassa is fused in an open vessel with oxide of bismuth; or by gently heating the oxide in a solution of chloride of potassa or soda: after washing with water, any unchanged protoxide is dissolved by a solution of 1 part of pure nitric acid in 9 of water. Arppe, who subsequently examined it (BERZELIUS, *Lehrbuch*), obtains it by dropping nitrate of bismuth into a solution of caustic potassa, boiling in the alkaline liquor, washing the precipitate, and, whilst moist, diffusing it through a solution of potassa into which chlorine is passed; a red precipitate is thus formed, which consists of bismuthic acid and oxide of bismuth, and which is to be digested in nitric acid of sufficient strength to dissolve the oxide; the remaining acid, which is a hydrate, is to be well washed and dried at 100° ; it is a red powder, becoming brown and anhydrous when dried at 266° ; at higher temperatures it begins to lose oxygen.

Bismuthic acid is decomposed by sulphuric acid, evolving oxygen, and forming sulphate of bismuth; dilute nitric acid neither dissolves nor decomposes it, but the strong acid expels oxygen and forms nitrate, especially when heated. With hydrochloric acid it yields chloride of bismuth and chlorine. When diffused through water, the hydrated bismuthic acid is also decomposed by chlorine, and a basic chloride is formed. Caustic potassa sparingly dissolves this acid, forming a red solution, from which water throws down a portion of bismuthate of potassa. Arppe describes several combinations of bismuthic acid with oxide of bismuth. Bismuthic acid consists of

							Arppe.
Bismuth	1	...	213	...	84.19	...	84.18
Oxygen	5	...	40	...	15.81	...	15.82
<hr/>							
Bismuthic acid.....	1		253		100.00		100.00

CHLORIDE OF BISMUTH, BiCl_3 , is procured by gently heating the metal in chlorine; it burns, and forms a grey compound. This chloride may also be prepared by heating 2 parts of corrosive sublimate with 1 of powdered bismuth, and expelling the excess of the former and the mercury by heat; or by evaporating the solution of oxide of bismuth in hydrochloric acid to dryness, and heating the residue in close vessels. Chloride of bismuth was formerly called *Butter of Bismuth*. It is of a grey

color, and fuses at about 480° . When exposed to air it deliquesces. It is decomposed by a large quantity of water, and yields a white deposit, which is an *oxychloride*. It consists of

						J. Davy.
Bismuth.....	1	213	66.35 66.4
Chlorine.....	3	108	33.65 33.6
<hr/>						<hr/>
Chloride of bismuth	1		321		100.00	100.0

OXYCHLORIDE OF BISMUTH, $\text{BiCl}_3, 2\text{BiO}_3$, is a white crystalline powder, formed by the action of water upon the chloride, or by precipitating nitrate of bismuth by chloride of sodium: it is soluble in hydrochloric acid, and soluble without decomposition in nitric acid. It consists of

Chloride of bismuth.....	1	321	40.04
Oxide of bismuth.....	2	474	59.96
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Oxichloride of bismuth	1		795		100.00

When a solution of 1 atom of chloride of bismuth and 2 of sal-ammoniac is evaporated, it yields prismatic crystals of an *ammonio-chloride of bismuth* $= 2\text{NH}_4\text{Cl} + \text{BiCl}_3$. (JACQUELAIN.)

CHLORATE OF BISMUTH. The solution of oxide of bismuth in chloric acid is decomposed when concentrated in vacuo; basic chloride of bismuth is deposited, and chlorous acid is disengaged. (WAECHTER.)

IODIDE OF BISMUTH, BiI_3 , obtained by heating iodine with the metal, is of a brown color, and insoluble in water. When hydriodic acid or iodide of potassium is added to nitrate of bismuth, a precipitate falls, of a deep-orange color, insoluble in water, but soluble in liquid potassa.

IODATE OF BISMUTH is thrown down upon adding iodate of potassium to nitrate of bismuth. It is white, and insoluble. (PLEISCHL.)

BROMIDE OF BISMUTH, BiBr_3 , is a grey compound, obtained by the direct action of bromine upon powdered bismuth. It fuses at about 400° , and sublimes at a low red-heat. It is decomposed by water, and oxide of bismuth is formed. (SERULLAS.)

BROMATE OF BISMUTH. When moist hydrated oxide of bismuth is digested in bromic acid, a white basic salt remains undissolved, not crystalline, and becoming anhydrous when dried at 310° ; it is rapidly decomposed at high temperatures. The hydrated salt is $= 3\text{BiO}_3, 2\text{BrO}_5, 6\text{HO}$. (RAMMELSBURG.)

FLUORIDE OF BISMUTH, BiF_3 , is soluble in water, and deposited, on evaporation, in the form of a white powder. (BERZELIUS.)

HYDRURET OF BISMUTH. When bismuth is made the negative electrode in water, black dendritical crystals are deposited upon it. (RUHLAND, *Schweigger's Journ.*, xv. 417.) According to Meurer, when bismuth is present during the energetic action of zinc on water or on hydro-

chloric acid, a small portion of it is carried off in the gaseous form: hence probably, the presence of arsenic has been erroneously suspected in samples of oxide or subnitrate of bismuth subjected to Marsh's test: but the stain of bismuth, under such circumstances, is pale grey, and insoluble in chloride of soda. (*Chem. Gaz.*, Feb. 1844.)

NITRATE OF BISMUTH. $\text{BiO}_3, 3\text{NO}_5, 9\text{HO}$. When nitric acid is poured upon powdered bismuth the action is intensely violent, and sometimes attended by ignition. Nitrate of bismuth is usually made by dissolving the metal to saturation in 2 parts of nitric acid and 1 of water; the action is rapid, and nitric oxide is copiously evolved: the solution affords deliquescent four-sided, prismatic crystals, which may be dissolved in a very small quantity of water, but if the solution, even when acid, be poured into a large quantity of water, it is decomposed. If characters be written on paper with nitrate of bismuth they are invisible when dry, but become white and legible on immersion in water, thus forming a *white sympathetic ink*. The same characters are rendered brown or black by solution of sulphuretted hydrogen. It is sometimes stated, that this and other salts of bismuth are blackened by exposure to light, but when such an effect ensues it depends probably upon their containing a minute portion of silver. The *crystallized nitrate* is a hydrated salt, composed of

						Berzelius.	Duflos.
Oxide of bismuth.....	1	237	49.38	48.8
Nitric acid	3	162	33.75	33.7
Water	9	81	16.87	17.5
<hr/>							
Crystals of nitrate of bismuth	1		480		100.00		100.0

When the preceding salt is decomposed by water, or by alkali not in excess, it affords a white and somewhat crystalline precipitate, commonly called *subnitrate of bismuth*, and formerly known as *Magistery of Bismuth*, *Pearl white*, and *Blanc d'Espagne*; it is insoluble in water, and when dried in the air is $= \text{BiO}, \text{NO}_5, \text{HO}$; but becomes anhydrous when adequately dried. By boiling in water, it yields, according to Duflos, a soluble acid salt, and leaves a more basic compound; and, according to Freundt, its composition varies with the mode of preparation. (*Chem. Gaz.*, March, 1844.) The following are the results of its analysis as given by Gmelin:

						Herberger.	Duflos.	Grouvelle.	R. Phillips.	Menigaud.
Oxide of bismuth	1	237	79	79.70	80.00
Nitric acid	1	54	18	14.44	13.58
Water	1	9	3	2.86	6.42
<hr/>										
	1		300		100		100.00		100.00	

SULPHURET OF BISMUTH, BiS_3 , is of a bluish color and metallic lustre; it is less fusible than bismuth, and is reduced by hydrogen at a red-heat, sulphuretted hydrogen being evolved. This sulphuret may be formed by fusion, and also by precipitating the salts of bismuth by sulphuretted hydrogen or alkaline hydrosulphurets, when it forms a black or dark brown precipitate, (hydrated,) which, when dried and heated, acquires metallic lustre. It blends with or is dissolved by the fused metal, in all proportions, but under these circumstances a crystalline sulphuret $= \text{BiS}_2$ is

sometimes formed, (WERTHER,) though frequently the tersulphuret again separates out of the fused mixture. It consists of

										H. Rose.	
										<i>Native.</i>	
						Lagerhielm.		J. Davy.			
Bismuth	1	...	213	...	81·6	...	81·619	...	81·8	...	80·98
Sulphur	3	...	48	...	18·4	...	18·381	...	18·2	...	18·92
<hr/>											
Sulphuret of bismuth	1		261		100·0		100·000		100·0		100·00

Native Sulphuret of Bismuth has been found in Cornwall, Bohemia, Saxony, and Sweden. It occurs massive and acicular, its lustre is metallic, and its color bluish-grey: its density is 6.4. It is a very rare mineral.

HYPOSULPHITE OF BISMUTH has not been examined.

SULPHITE OF BISMUTH is an insoluble white powder, which is not taken up by excess of the acid. (FOURCROY.)

HYPOSULPHATE OF BISMUTH has not been examined.

SULPHATE OF BISMUTH, $\text{BiO}_3, 3\text{SO}_3$, is obtained by heating powdered bismuth in sulphuric acid. It is a white compound, insoluble in, but decomposed by water, which converts it into a *subsulphate* and *supersulphate*. The *sulphate* consists of

					Lagerhielm.	Thomson.			
Oxide of bismuth	1	...	237	...	66·39	...	66·35	...	66·67
Sulphuric acid.....	3	...	120	...	33·61	...	33·65	...	33·33
<hr/>									
Sulphate of bismuth	1		357		100·00		100·00		100·00

The *subsulphate* consists of

					Berzelius.		
Oxide of bismuth	1	...	237	...	85.56	...	85.5
Sulphuric acid	1	...	40	...	14.44	...	14.5
<hr/>			<hr/>		<hr/>		<hr/>
Subsulphate of bismuth	1		277		100.00		100.0

The *supersulphate* yields acicular hydrated crystals, and when evaporated a very deliquescent saline mass remains.

SELENIURET OF BISMUTH. When bismuth and selenium are heated together, they combine with slight ignition, and form a silver-white crystalline compound. (BERZELIUS.)

PHOSPHURET OF BISMUTH does not, according to Pelletier, exist; at least, it cannot be formed by the usual process of projecting phosphorus upon the hot metal. When phosphuretted hydrogen gas is passed into nitrate of bismuth, a dark-brown precipitate ensues, which, heated in close vessels, loses the whole of its phosphorus.

PHOSPHITE OF BISMUTH. The solution of terchloride of phosphorus with excess of ammonia, gives a white precipitate in the solution of oxide of bismuth in hydrochloric acid, which when heated in a retort, evolves pure hydrogen. (II. ROSE.)

PHOSPHATE OF BISMUTH is formed, according to Wenzel, by digesting the oxide in phosphoric acid; an insoluble subphosphate, and a soluble and crystallizable phosphate, are the results.

CARBONATE OF BISMUTH is thrown down from the nitrate by carbonated alkalis; it is a white powder, insoluble in water and in carbonic acid, and soluble in nitric acid with effervescence; when dried (in the air?) it consists of

				Thomson.
Oxide of bismuth	1	...	237 83.0
Carbonic acid	1	...	22 7.6
Water	3	...	27 9.4
<hr/>				
Carbonate of bismuth	1		286	100.0

CYANIDE OF BISMUTH has not been formed. *Ferrocyanide of bismuth*, formed by double decomposition, is a white or yellowish powder, soluble in nitric acid, and precipitated again by water. (ITTNER.) The ferridcyanide of potassium produces a brown precipitate in nitrate of bismuth.

BORATE OF BISMUTH is a white powder, nearly insoluble in water.

ALLOYS OF BISMUTH. Bismuth readily unites with *potassium*: Serullas obtains this alloy by heating together a mixture of 120 parts of bismuth, 60 of charred bitartrate of potassa, and 1 of nitre; these substances should be well rubbed together and fused in a covered crucible. The alloy decomposes water, and when broken and exposed to air, fuses, and even ignites. We know little of the other alloys of bismuth, excepting those which it forms with *tin* and *lead*, and which are remarkable for the low temperature at which they enter into fusion, and for the extraordinary irregularities of expansion and contraction which they exhibit with changes of temperature, and which have been examined by Ermann. An alloy of 2 parts of bismuth, 1 of lead, and 1 of tin, fuses at 200°. (ROSE.) The alloy of 8 parts of bismuth, 5 of lead, and 3 of tin fuses at a little below 212°: the addition of 1 part of mercury renders it still more fusible, and this compound is sometimes cast for amusement into the form of tea-spoons, which run down when dipped into boiling water. It may also be employed for taking casts from medals, and even from the surface of wood and embossed paper: some beautiful casts have also been made in this metal of the internal ear, showing the complexities of its bony cavities. When this alloy is poured upon a marble slab, and broken as soon as it is cool enough to be handled, its surfaces are bright and conchoidal, and the whole extremely brittle: after this it becomes very hot, and loses its brittleness, its fractured surface becoming granular and dull: it is evident that this change of temperature must arise from some new molecular arrangement of the particles, after solidification, and is not referable to the evolution of latent heat arising out of the solidification of the interior after that of the exterior crust, as Berzelius has suggested (*Traité de Chimie*.) From Warrington's experiments on this subject, it appears, that on allowing the metal (the fusing-point of which was 202°) to concrete in a small platinum crucible with an immersed thermometer,

it sometimes fell to 90° , and then rose to 150° , giving an evolution of heat = 60° . (*Mem. Chem. Soc.*, Jan. 1842.)

Ermann's experiments above alluded to, were made with Rose's fusible alloy (*Ann. Ch. et Ph.*, XL. 197): the general results have already been adverted to under the head of "Expansion by heat" (p. 31). The following table abridged from Ermann, gives them more in detail:

Temperature of the Alloy.		Volume of the Alloy.		Temperature of the Alloy.		Volume of the Alloy.	
Reaum.	Fahr.			Reaum.	Fahr.		
0°	32°	100,000	60°	166°	99,389
10	54	100,192	65	178	99,478
20	76	100,443	70	180	100,000
30	99	100,803	75	201	100,862 fuses
35	111	100,830 max.	80	212	101,792
40	122	100,679	100	257	102,217
45	133	100,120	120	302	102,599
50	146	99,480	130	324	102,784
55	156	99,291 min.	140	346	103,072

CHARACTERS OF THE SALTS OF BISMUTH. Many of them are resolved by water into a soluble acid salt, and a less soluble or insoluble and more basic compound. In the clear acid solutions of oxide of bismuth, potassa, soda, and ammonia, and their carbonates, produce white precipitates, insoluble in excess of the alkali. Phosphate of soda occasions a white precipitate in these salts: tincture or infusion of galls, a brown precipitate. Hydrosulphuret of ammonia and sulphuretted hydrogen produce brown or black precipitates, easily reduced to metallic bismuth when mixed with soda, and fused in the inner flame of the blow-pipe. Chloride and nitrate of bismuth are decomposed by the immersion of plates of zinc, cadmium, tin, iron, and lead: the metal is commonly thrown down in the form of a black crystalline powder, except by iron, which at first produces it with metallic lustre. Before the blow-pipe, oxide of bismuth melts readily into a brown glass, which becomes brighter as it cools. With microcosmic salt it forms a grey-yellow glass, which loses its transparency, and becomes pale when cool: add a further proportion of oxide and it becomes opaque. With borax it forms a grey glass, which decrepitates in the interior flame, and the metal is reduced and volatilized. It is readily reduced by itself on charcoal.

§ XIX. URANIUM. U. 60.

THIS metal was discovered in 1789, by Klaproth, in a mineral termed *Pechblende*, which is a very impure oxide of uranium, but from which the metal and its compounds are almost exclusively obtained. In combination with phosphoric acid it exists in the varieties of *uranitic mica*, found in France, and in great beauty at Callington in Cornwall. A native oxide, and a sulphate, also occasionally occur, but all these are rare minerals. The protoxide of uranium was for a long time regarded as the metal, till in 1841, Peligot pointed out the error, and first obtained pure uranium.

The principal information upon the subject of uranium and its compounds will be found in the memoirs of Peligot (*Ann. Ch. et Ph.*, N.S.,

v. 35); Ebelmen (*ibid.*, v. 47 and 189); Wertheim (*ibid.*, Mai, 1844); and Berzelius (*Handbuch*). Gmelin has given an excellent summary derived from these sources, and the crystalline forms of several of the uranic salts have been investigated by Provostaye. (*Ann. Ch. et Ph.*, v.)

Uranium is procured by the decomposition of its chloride by potassium, the process being similar to that by which magnesium is obtained from the chloride of magnesium. The action is very intense, and the platinum crucible is generally acted on, so that an iron vessel is sometimes substituted. When the action is over and the crucible has cooled, its contents are washed out with cold water: the metal remains in the form of a black powder, not acted on at common temperatures by air or water, but when it is gently heated, it burns with much brilliancy into oxide. It is dissolved by dilute acids with the evolution of hydrogen. Uranium may also be obtained by adding equal parts of sal-ammoniac and common salt to a solution of uranate of ammonia in hydrochloric acid, evaporating to dryness, and fusing the residue in a covered crucible: when cold the product is dissolved in cold water and the uranium remains. (WÖHLER.)

URANIUM AND OXYGEN. There are 5 oxides of uranium. 1. Suboxide, U_4O_3 . 2. Protoxide, UO . 3. Black oxide, U_4O_5 . 4. Green oxide, U_3O_4 . 5. Peroxide (Sesquioxide or uranic acid), U_2O_3 . The equivalent of uranium is 60. (60 GMELIN; 61 PELIGOT; 59·43 EBELMEN; 59·71 WERTHEIM; 64·2 BERZELIUS.)

SUBOXIDE OF URANIUM, U_4O_3 , is precipitated as a *hydrate* by adding ammonia to a solution of the corresponding subchloride $=U_4Cl_3$: it is at first brown, but almost immediately begins to evolve hydrogen, and pass into a higher state of oxidizement; and if exposed to air, uranate of ammonia is ultimately formed. (PELIGOT.)

PROTOXIDE OF URANIUM. UO . This was formerly regarded as metallic uranium: it is obtained by heating peroxalate of uranium out of contact of air, or by passing a stream of hydrogen over it (or over the green oxide) at a red-heat. It is grey or brown, sometimes crystalline, and having metallic lustre. Alkalis precipitate it from its solutions in the form of a brown gelatinous hydrate, in which state it dissolves in the acids, forming green salts which, under the influence of air or oxidizing agents, pass into persalts. By the carbonated alkalis it is thrown down as a green hydrated precipitate, soluble in excess of the carbonate and especially in carbonate of ammonia. It consists of

Uranium	1	60	88·24
Oxygen	1	8	11·76
<hr/>					
Protoxide of uranium	1		68		100·00

BLACK OXIDE OF URANIUM, U_4O_5 , is the result of the exposure of the green oxide, or of nitrate of uranium, to a strong red-heat: it should be cooled out of contact of air: it does not form definite salts, and is regarded by Ebelmen as a mixture of UO , and U_3O_4 , or of protoxide and green oxide. Its components are

Uranium	4	240	85.71	} = {	Protoxide	2	136	48.57
Oxygen	5	40	14.29		Green oxide	1	144	51.43
<hr/>								
Black oxide of uranium }	1	280	100.00			1	280	100.00

GREEN OXIDE OF URANIUM. (*Oxydoxydule?*) U_3O_4 . This was formerly regarded as the protoxide: it is the result of the combustion both of the metal and of the protoxide, and is also obtained by subjecting the peroxide to a red-heat. The usual source of this oxide, and of the compounds of uranium in general, is *pechblende*, which in its purest state contains from 60 to 70 *per cent.* of green oxide; but it is generally a very complicated mineral, and consequently the processes for the separation of pure oxide of uranium are delicate and tedious; the usual substances accompanying it are sulphur, selenium, phosphoric acid, lime, magnesia, alumina, silica, vanadium, manganese, arsenic, bismuth, antimony, zinc, tin, lead, iron, cobalt, nickel, copper, and silver. I shall here detail the methods recommended by Arfwedson and Peligot, referring to Ebelmen (*Ann. Ch. et Ph.*, N.S., v. 189); Laugier (*Journ. der Pharm.*, ix. 145); and Werner (*Journ. der Prakt. Chem.*) for other modes of operation. Arfwedson dissolves the powdered *pechblende* (I have always found it advantageous previously to roast it in coarse powder under a muffle, as long as fumes escape) in warm nitrohydrochloric acid, pours off the solution, drives off excess of acid by evaporation, dilutes with water, filters, and passes sulphuretted hydrogen through the filtrate (so as to precipitate arsenic, lead, copper, bismuth, and tin), filters again, and heats the liquor to expel excess of sulphuretted hydrogen, a little nitric acid being added to ensure the peroxidizement of iron; he then supersaturates it with considerable excess of carbonate of ammonia, which throws down lime and oxide of iron, as well as most of the oxide of zinc and of cobalt, but retains the oxide of uranium in solution, as well as small portions of cobalt and zinc: the ammoniacal solution is then filtered and boiled as long as carbonate of ammonia is given off, so as to throw down the oxides of uranium, cobalt, and zinc, with the exception of a trace of oxide of cobalt, which gives the liquor a pink tint. The precipitated oxides are then washed, dried, and heated to redness till they become very dark green: lastly, they are digested in cold dilute hydrochloric acid for several hours, which abstracts the cobalt and zinc, and leaves pure green oxide of uranium.

Peligot proceeds as follows: the selected *pechblende* is roasted and digested in nitric acid; the solution thus obtained is filtered, evaporated to dryness, and the dry residue dissolved in water, which gives a green solution, leaving oxide and arseniate of iron and sulphate of lead: the green solution is duly evaporated, and gives crystals of nitrate of uranium, which are put into a funnel and washed with a little cold water, dried, and shaken in a bottle with ether; the yellow ethereal solution is left to spontaneous evaporation, and the remaining salt dissolved in hot water and again crystallized: these crystals, exposed to a red-heat, leave the green oxide.

This oxide is of a deep dull-green color, or nearly black when in lumps: when intensely heated it loses a little oxygen, and by hydrogen, sulphur, or carbon, is converted into protoxide. When it is precipitated

from its solutions by ammonia, it falls in the form of a dirty green or brown *hydrate*, $U_3O_4 \cdot 3HO$, which digested in carbonate of ammonia, is resolved into peroxide which is dissolved, and into a brown hydrate of the protoxide which remains undissolved. In the state of recently-precipitated hydrate it is readily soluble in the acids, but less so after it has been ignited. The solutions have the properties of mixed solutions of protoxide and peroxide: thus alcohol throws down a sulphate of the protoxide from the solution of this green oxide in sulphuric acid, whilst a sulphate of the peroxide, of a pure yellow color, remains in solution. The green oxide consists of

Uranium	3	...	180	...	84.91	} = {	Protoxide	1	...	68	...	32.08
Oxygen	4	...	32	...	15.09		Peroxide	1	...	144	...	67.92
<hr/>												
Green oxide of uranium }	1		212		100.00				1		212	100.00

PEROXIDE OF URANIUM. U_2O_3 . Uranium and its inferior oxides pass into peroxide when acted upon by nitric acid, forming a yellow solution, from which the alkalis throw down compounds of the peroxide with the precipitants. A pure hydrate of the peroxide may, however, be obtained by evaporating the alcoholic solution of the pernitrate till it effervesces in consequence of the escape of nitrous ether; the yellow residue, washed first with cold and then with hot water, leaves the *hydrate*, assuming, when dried at 212° , the form of a yellow powder = $U_2O_3 \cdot HO$, but if dried in *vacuo* = $U_2O_3 \cdot 2HO$. Its sp. gr. is 5.9. At a high temperature (about 570°) it becomes anhydrous, and afterwards loses oxygen, and leaves a brown mixture of protoxide and green oxide: in its anhydrous state it is red, and consists of

Uranium	2	...	120	...	83.33
Oxygen	3	...	24	...	16.67
<hr/>					
Peroxide of uranium	1		144		100.00

As most of the salts of this oxide contain 1 atom of it combined with 1 atom of acid, Peligot assumes U_2O_2 as its *base* (under the name of *Uranyle*,) and represents it by $U_2O_2 + O$.

The salts of the peroxide of uranium are best formed by the action of air or nitric acid upon the salts of the lower oxides: they may be obtained in a less pure state by dissolving its compounds with the alkalis (uraniates) in acids. They are yellow and mostly soluble in water, and are reduced to protosalts by sulphuretted hydrogen, and by alcohol and ether under the influence of solar light. They are precipitated by ammonia, potassa, and soda, and the precipitates (alkaline uraniates) are insoluble in excess of alkali; when precipitated by the alkaline carbonates the precipitate does redissolve, especially if bicarbonates are used. With the alkaline hydrosulphurets they give dark-brown or black precipitates; with oxalic acid and the oxalates yellow precipitates; and yellow with the alkaline succinates; brown with tincture of galls; and a characteristic reddish-brown (much resembling the effect with copper-salts) with ferrocyanide of potassium.

But peroxide of uranium also unites to bases, forming *uraniates*: those of the alkalis are obtained by precipitating the uranic salts with

them. The uranates of baryta, lime, magnesia, &c., are formed by mixing their salts with those of the uranic oxide, and adding ammonia, but a portion of uranate of ammonia in these cases goes down with them.

Uranate of Ammonia, $\text{NH}_4\text{O}, 2\text{U}_2\text{O}_3$, falls on mixing nitrate of uranium with excess of ammonia; it is a yellow hydrated powder which may be dried at 212° without decomposition. At higher temperatures it loses ammonia, water, and nitrogen, and leaves protoxide: it is insoluble in excess of ammonia and in water containing sal-ammoniac; but in pure water it is to a small extent soluble. It dissolves in sesquicarbonate of ammonia, and the solution affords yellow prismatic crystals of *hydrated uranio-carbonate of ammonia* $= 2[\text{NH}_4\text{O}, \text{CO}_2] + \text{U}_2\text{O}_3, \text{CO}_2$. (EBELMEN); when these crystals are heated to about 570° , they are entirely decomposed, and leave pure peroxide of uranium: when rapidly heated in close vessels, protoxide of uranium is produced, which burns into green oxide on admission of air. This salt is very sparingly soluble in pure water, but dissolves readily in that which contains carbonate of ammonia: when this solution is boiled, it deposits a pale yellow powder which appears to be a basic salt.

Uranate of potassa, $\text{KO}, 2\text{U}_2\text{O}_3$, is a pale orange-colored powder, which falls on adding excess of potassa to nitrate of uranium; when heated it loses water and acquires a deeper hue. In its hydrated state it readily dissolves (in carbonate, and especially) in bicarbonate of potassa, and the solution yields crystalline crusts of *uranio-carbonate of potassa* $= 2[\text{KO}, \text{CO}_2] + \text{U}_2\text{O}_3, \text{CO}_2$. This salt is soluble in 13.5 parts of water at 60° , and insoluble in alcohol. (EBELMEN.)

Uranate of soda, $\text{NaO}, 2\text{U}_2\text{O}_3$, resembles the potassa salt, and affords a similar *uranio-carbonate*.

Uranate of lime falls on adding ammonia to a mixed solution of nitrate of uranium and lime, but the pure salt has not been examined.

Uranate of baryta, $\text{BaO}, 2\text{U}_2\text{O}_3$, is formed by precipitating nitrate of uranium by baryta water, and washing the precipitate till free from excess of baryta: it is an orange-colored powder.

Uranate of magnesia, $\text{MgO}, 2\text{U}_2\text{O}_3$, is obtained by heating to redness the uranio-acetate of magnesia. (WERTHEIM.) When ammonia is added to a mixed solution of nitrate of uranium and magnesia, the precipitate contains uranate of ammonia.

CHLORIDES OF URANIUM. *Protochloride of Uranium*, UCl , is obtained by passing dry chlorine over a mixture of oxide of uranium with one-fourth its weight of carbon heated to redness in a glass or porcelain tube: red vapors of the chloride are formed, which condense in the cooler part of the tube into dark-green octohedral crystals: they dissolve rapidly in water, furnishing a dark-green solution, and when exposed to air, evolve fumes of hydrochloric acid. On evaporating the aqueous solution, a green uncrystallizable deliquescent substance remains, apparently differing from the original chloride. When a stream of dry hydrogen is passed over protochloride of uranium heated nearly up to its temperature of vaporization, till hydrochloric acid is no longer evolved, a dark-brown *subchloride* $= \text{U}_4\text{Cl}$ is formed ($4\text{UCl} + \text{H} = \text{U}_4\text{Cl} + \text{HCl}_3$.) It gives a purple solution with water, which presently evolves hydrogen, a dark-red oxide falls, and a green solution of the protochloride remains. (PELIGOT.)

OXICHLORIDE OF URANIUM. When dry chlorine is passed over red-hot protoxide of uranium, orange-colored vapors are formed, which condense into a yellow crystalline, fusible, deliquescent, and not very volatile substance $= 2\text{UO}_2\text{Cl}$ or $\text{U}_2\text{O}_2\text{Cl}$: this is Peligot's *chloride of uranyle*. When heated with potassium, it yields chloride of potassium and protoxide of uranium. $2\text{UO}_2\text{Cl} + \text{K} = 2\text{UO}_2 + \text{KCl}$.

The protochloride and oxichloride of uranium both combine with ammonia, forming $\text{NH}_3, 3\text{UCl}_4$ (RAMMELSBERG,) and $\text{NH}_4\text{Cl} + \text{U}_2\text{O}_2\text{Cl} + \text{HO}$. (PELIGOT.) Peligot has also described a compound of the oxichloride of uranium with chloride of potassium $= \text{KCl}, \text{U}_2\text{O}_2\text{Cl}$: it crystallizes with 2 atoms of water.

CHLORATE OF URANIUM. The green solution of hydrated protoxide of uranium in chloric acid evolves chlorine and becomes yellow, from the formation of hydrochlorate of the peroxide: its solution in perchloric acid undergoes similar changes.

IODIDE OF URANIUM. Hydrated protoxide of uranium dissolves in hydriodic acid, forming a dark-green solution, which deposits, on spontaneous evaporation, a black crystalline compound soluble in water.

IODATE OF URANIUM. Iodate of soda produces a pale-green precipitate in the hydrochloric solution of protoxide of uranium: it gradually passes into white iodate of the peroxide, which is sparingly soluble in water, and which falls when iodic acid or iodate of potassa is added to nitrate of uranium. Periodate of potassa gives a grey-green precipitate with solution of protochloride of uranium, which becomes yellowish-white by passing into periodate of the peroxide. (RAMMELSBERG.)

BROMIDES OF URANIUM. When the dark-green solution of hydrated protoxide of uranium in hydrobromic acid is evaporated over oil of vitriol in vacuo, it deposits dark-green crystals, and dries into a very deliquescent mass $= \text{UBr}_4, 4\text{HO}$.

When protoxide of uranium is boiled with bromine and water, or when peroxide of uranium is dissolved in hydrobromic acid, a colorless solution is formed which becomes yellow on evaporation, and yields yellow deliquescent prismatic crystals.

When sulphate of peroxide of uranium is decomposed by its equivalent of bromate of baryta, and the yellow filtrate evaporated in vacuo, a clear syrupy liquor is obtained, which, heated in a water-bath, evolves bromine, and at last concretes: re-dissolved and re-evaporated, a yellow pulverulent hydrated *bromate of uranium* is ultimately obtained $= 4\text{U}_2\text{O}_3, 3\text{BrO}_5, 16\text{HO}$. (RAMMELSBERG.)

FLUORIDE OF URANIUM. UF_4 . The yellow solution of peroxide of uranium in hydrofluoric acid yields, on evaporation, a white uncrystallizable residue. This salt combines with the alkaline fluorides, forming soluble and crystallizable compounds. (BERZELIUS.)

NITRATE OF URANIUM. $\text{U}_2\text{O}_3, \text{NO}_5, 6\text{HO}$. This is the common crystallized nitrate of uranium obtained by evaporating the nitric solution

of any of the oxides: it forms yellow prisms efflorescing in a warm atmosphere or in vacuo into a terhydrate. When heated it fuses in its water of crystallization, becoming orange-colored, and at a red-heat leaves green oxide. It is very soluble in water, alcohol, and ether. When its alcoholic solution is gently heated (to about 100°) it effervesces and evolves nitrous ether, depositing a yellow powder, which is nearly pure hydrated peroxide. Its ethereal solution exposed to the sun's rays deposits green oxide, nitrous ether and a green solution of protoxide being at the same time formed. (BUCHOLZ.) When crystallized nitrate of uranium is carefully heated till it becomes orange-colored, a yellow insoluble *subnitrate* separates, containing 92 *per cent.* of oxide: this, at a red-heat, passes first into U_3O_4 , and then into U_2O_3 . (PELIGOT.)

URANIUM AND SULPHUR combine with the evolution of heat and light when fused together. Rose obtained a yellowish-black protosulphuret by passing the vapor of sulphuret of carbon over the green oxide heated to redness in a porcelain tube. Sulphurets of uranium also appear to be thrown down as black and brown hydrates, by adding alkaline hydrosulphurets to the solutions of the oxides, but the atomic constitution of these precipitates has not been accurately determined.

SULPHITES OF URANIUM. Sulphite of soda gives a greyish-green precipitate in the hydrochloric solution of protoxide of uranium, sulphurous acid being at the same time evolved. The precipitate is soluble in acids, and is $=2UO,SO_2,2HO$. When the solution of the ammonio-carbonate of peroxide of uranium in sulphurous acid is boiled, or when sulphite of ammonia is added to nitrate of uranium, a yellow granular precipitate falls which is a sulphite of the peroxide. (BERTHIER.)

SULPHATES OF URANIUM. A *sulphate of protoxide of uranium*, UO,SO_3 , is formed by dissolving the protoxide in hot sulphuric acid, or by adding sulphuric acid to the concentrated aqueous solution of the protochloride: it forms green hydrated crystals, which do not become anhydrous till so highly heated as to begin to lose acid, and which in a large quantity of water are resolved into a green acid solution, and a deposit of basic sulphate $=2UO,SO_3,2HO$, when dried in vacuo. This salt forms a crystallizable double sulphate with sulphate of ammonia, $=NH_4O,SO_3,+UO,SO_3$.

Sulphate of green oxide of uranium (protopersulphate) is formed by dissolving the green oxide in sulphuric acid, and expelling the excess of acid by heat in a platinum crucible: it is a pale-green mass which may be $=U_3O_4,2SO_3$, or $UO,SO_3,+U_2O_3,SO_3$. When heated up to redness it evolves sulphurous acid, and leaves a pale-yellow sulphate of the peroxide: $2[U_3O_4,2SO_3]=3[U_2O_3,SO_3]+SO_2$.

Sulphate of peroxide of uranium, U_2O_3,SO_3 , is obtained by oxidizing the solution of the green oxide in sulphuric acid by nitric acid, or by adding sulphuric acid to a solution of the nitrate, evaporating to dryness so as to expel excess of acid, dissolving the residue in water, and concentrating the solution by evaporation to the consistency of syrup: it is slowly and difficultly crystallizable in small yellow prisms $=U_2O_3,SO_3,3HO$: dried at 212° , they lose 2 atoms of water, and become anhydrous

at about 570° , in which state, if exposed to air, 3 atoms of water are again absorbed: at a red-heat the acid and some oxygen are expelled, and green oxide remains. This salt is very soluble in water, and it dissolves in 25 of cold and 20 of boiling alcohol. (EBELMEN.) A solution of this sulphate in dilute sulphuric acid yields crystals of a *bisulphate*, and if dissolved in concentrated sulphuric acid crystals of *tersulphate* may be obtained. (BERZELIUS.)

AMMONIO-PERSULPHATE OF URANIUM, $\text{NH}_4\text{O},\text{SO}_3; \text{U}_2\text{O}_3,\text{SO}_3 + 2\text{HO}$, crystallizes out of a mixed solution of the two sulphates. (PELIGOT.)

POTASSIO-PERSULPHATE OF URANIUM, $\text{KO},\text{SO}_3; \text{U}_2\text{O}_3,\text{SO}_3; + 2\text{HO}$, forms small yellow crystals on evaporating the mixed solution of the component sulphates; they become anhydrous at 250° , and may be fused at a red-heat without decomposition. This salt is soluble in 9 parts of water at 70° , and in about 5 parts at 212° ; it is insoluble in alcohol. (BERZELIUS.)

SELENITE OF PEROXIDE OF URANIUM, when neutral, is a yellow powder; when dissolved in aqueous selenious acid, it yields on evaporation an imperfectly crystalline residue of an acid selenite. (BERZELIUS.)

PHOSPHATES OF URANIUM. When excess of phosphate of soda is added to the hydrochloric solution of protoxide of uranium, a gelatinous green precipitate falls which is soluble in concentrated hydrochloric acid, but falls again on dilution: its formula is $2\text{UO},\text{HO},\text{cPO}_5 + 2\text{HO}$. (RAMMELSBERG.) A phosphate of the peroxide of uranium $= 2\text{U}_2\text{O}_3, \text{PO}_5, 10\text{HO}$, is thrown down by phosphoric acid from a solution of peracetate of uranium: it may also be obtained by adding ammonia to a solution of the peroxide in excess of phosphoric acid: it is pale yellow, and scarcely soluble in water, but readily soluble in carbonate of ammonia. (LAUGIER. *Ann. Ch. et Ph.*, xxiv. 239.)

The *uranite* of Autun is a hydrated double phosphate of peroxide of uranium and lime $= \text{CaO}, 2\text{U}_2\text{O}_3, \text{PO}_5, 8\text{HO}$: in *chalkolite*, the lime is replaced by oxide of copper. (PELIGOT.) See also an analysis of artificial uranite by Mr. Cock. (*Proc. Chem. Soc.*, March, 1842.)

CARBONATE OF URANIUM. When nitrate of uranium is precipitated by a carbonated alkali the product probably contains a percarbonate, but it loses carbonic acid on drying: hydrated peroxide of uranium dissolved in aqueous carbonic acid is thrown down unchanged on heating the solution. When *ammonio-carbonate of uranium* is gently heated, an orange-colored powder remains, which is a carbonate of the peroxide. (LECANU.) When the precipitate of uraniate of ammonia obtained by adding excess of ammonia to the nitrate of uranium, is dissolved in sesquicarbonate of ammonia, the solution on cooling, or spontaneous evaporation, affords yellow crystals $= 2[\text{NH}_4\text{O},\text{CO}_2] + \text{U}_2\text{O}_3,\text{CO}_2$. (EBELMEN.) When these crystals are carefully heated they lose carbonate of ammonia, and leave carbonate of uranium; at higher temperatures red anhydrous peroxide of uranium is the result. When rapidly heated out of contact of air, this salt leaves protoxide of uranium, which

is pyrophoric, and burns in the air into green oxide. The crystals of this ammonio-carbonate are soluble, according to Ebelmen, in 20 parts of water at 60°; but according to Berzelius, they are insoluble in pure water, and only dissolve in water holding carbonate of ammonia in solution. When boiled with water they evolve carbonate of ammonia, and deposit an insoluble basic salt.

There appears to be no carbonate of protoxide of uranium, for although the green precipitate formed by adding carbonate of ammonia to solutions of the protosalts of uranium is soluble in excess of the carbonate, yet the solution, when evaporated, gives off carbonic acid, and deposits hydrated oxide. Carbonate of ammonia throws down a pale-green precipitate from a solution of the sulphate of the green oxide, which is also soluble in excess of the ammoniacal carbonate, but on applying heat, the green oxide falls free from carbonic acid.

CYANIDE OF URANIUM. Cyanide of potassium occasions a yellow precipitate in solutions of peroxide of uranium.

FERROCYANIDE OF URANIUM. Ferrocyanide of potassium produces a very characteristic bright reddish-brown precipitate, with the yellow salts of uranium: it bears a close resemblance to the corresponding copper compound.

CHARACTERS OF THE SALTS OF URANIUM. These will be evident from the preceding details: their peculiar yellow color, and that of the precipitates by the alkalis, when they contain the peroxide; the green tint of the protosalt becoming yellow by oxidizement, while the yellow salts become green by certain deoxidizing agents; the rich reddish-brown precipitate by ferrocyanide of potassium, and the brown precipitate by infusion of galls, are very distinctive properties.

Uranium is not precipitated from its solutions by sulphuretted hydrogen, nor is it thrown down in a metallic state by any of the other metals. Before the blow-pipe the peroxide of uranium becomes green or greenish-brown. With microcosmic salt in the interior flame it forms a clear yellow glass, the color of which becomes more intense when cold. If long exposed to the exterior flame, and frequently cooled, it gives a pale yellowish-red or brown glass, which becomes greenish as it cools. With borax in the interior flame, a clear, colorless, or faintly-green glass is formed, containing black particles which appear to be the metal in its lowest state of oxidation. In the exterior flame this black matter is dissolved, if the quantity be not too great, and the glass becomes bright yellowish-green, and after further oxidation yellowish-brown. If brought again into the interior flame, the color gradually changes to green, and the black matter is again precipitated, but no further reduction takes place.

Peroxide of uranium is used to give a yellow, and a greenish-yellow, to glass: green oxide has been used in the Berlin porcelain manufactory to produce a black color. It is probable that some of the salts of uranium might be available in the art of calico-printing and as sources of pigments, but the scarcity of the metal at present precludes these applications.

§ XX. TITANIUM. Ti. 24.

TITANIUM was first recognised as a distinct substance by Gregor, in 1791; he detected it in a mineral found in the form of a black sand in the vale of Menachan, in Cornwall. Some of its compounds were afterwards examined by Klaproth, in 1795, who named it *Titanium*, after the Titans of ancient mythology. (See his Analysis of the Red Schorl of Hungary, *Beiträge*, i. 233.) For our knowledge of the properties of *Titanium* in its metallic state we are chiefly indebted to Wollaston, who discovered it in small cubic crystals, having the lustre of burnished copper, in the slag of the iron-furnaces at Merthyr Tydvil, in South Wales. (*Phil. Trans.*, 1823, p. 17.) These crystals, which have been found in similar slags from other sources, are titanium, almost absolutely pure. They have the following properties: they are so hard as to scratch rock-crystal; sp. gr. 5.3; they are not acted on by nitric, hydrochloric, or sulphuric acids, nor are they soluble in nitrohydrochloric acid. Before the blow-pipe they are infusible; they are, however, superficially oxidized by a continued heat, becoming of a purple or red color. Borax has no action on them, but only removes the superficial oxide. Nitre oxidizes them on the surface. The combined action of nitre and borax soon effects their solution; but as these salts do not unite by fusion, the addition of soda accelerates their action. The fused mass becomes opaque on cooling, by the deposit of a white oxide, which may either be previously freed of the salts by boiling water, and then dissolved in hydrochloric acid, or the whole mass may be at once dissolved together. In either case alkalis precipitate from the solution a white oxide, insoluble in excess of alkali, either pure or carbonated. By evaporating the hydrochloric solution to dryness at 212° , it is freed of redundant acid, and a soluble chloride remains, in a favorable state for exhibiting the characteristic properties of the metal.

Titanium exists in the state of nearly pure peroxide, or as titanitic acid, in the minerals called *rutile*, *anatase*, and *oysanite*, which occur in Bavaria, Norway, Switzerland, and in the valley of Oysans, in France. *Titanite* is a silicate of titanium and lime; it is of a brown color, and occurs imbedded in the quartz and granite of primitive countries, and sometimes traverses rock-crystal in fine hair-like filaments. In this country, it occurs at Beddgelert, in Caernarvonshire; and near Killin, in Scotland. The finest specimens are those from the vicinity of Mont Blanc and St. Gothard.

Menachanite consists principally of oxides of titanium and iron; it is found in small grains, somewhat resembling coarse gunpowder, in the bed of a stream at Menachan, in Cornwall.

According to Laugier (*Ann. de Chim.*, lxxxix. 306), the metal may be obtained from *titanite* by fusion with potassa; the fused mass, washed with water, leaves oxide of titanium, containing a little iron; it is to be dissolved in hydrochloric acid, and precipitated by oxalic acid. The oxalate affords the metal by intense ignition with charcoal; it is, however, not possible to obtain it in any state of agglutination. From *menachanite*, peroxide of titanium may be obtained by fusing it with potassa, and adding hydrochloric acid to the alkaline solution, so as merely to neutralize the alkali and precipitate the oxide: to separate a

little adhering iron, this must be dissolved in excess of hydrochloric acid, and precipitated by oxalic acid as before.

Liebig prepares metallic titanium by putting fragments of recently-made ammonio-chloride of titanium into a glass tube, half an inch wide and two or three feet long, transmitting through it a current of perfectly dry ammonia, and, when atmospheric air is entirely displaced, applying heat until the glass softens: complete decomposition ensues, nitrogen gas is disengaged, hydrochlorate of ammonia sublimes, and metallic titanium is left in the state of a dark blue-colored powder. If exposed to the air while warm, it is apt to take fire. (TURNER.)

The equivalent of titanium has not been very satisfactorily determined; deduced from the experiments of H. Rose it is 24.29, and from those of Mosander, 23.66. Gmelin adopts the number 24, which is about the mean of these results. (24.3, GRAHAM. 26, THOMSON.)

PROTOXIDE OF TITANIUM. Ti O . Titanium appears to be susceptible of two degrees of oxidizement. When the peroxide or titanous acid is intensely heated with charcoal, or when it is subjected to a white-heat in a charcoal crucible, it is superficially reduced; but the interior is in the state of a black powder, which some have regarded as a protoxide. When a plate of zinc is immersed in a solution of chloride of titanium, a purple powder is obtained, which appears to contain the protoxide: it is also formed when the vapor of potassium is passed over heated titanous acid: it is infusible and unchanged by heat alone, but when exposed to the joint action of heat and air it passes into titanous acid. It is very sparingly soluble in hydrochloric acid, which yields a blue solution: boiling sulphuric acid dissolves it more copiously, and the solution, when saturated, is deep blue: it forms a double salt with ammonia; boiled with nitric or nitrohydrochloric acid it is converted into titanous acid. There are, however, considerable doubts as to the real nature of this oxide. Rose found, on heating titanous acid with zinc filings in a covered crucible till the excess of zinc had sublimed, that a black powder remained after the action of hydrochloric acid on the residue, which, however, became white when heated red-hot with access of air, but yet did not increase in weight.

PEROXIDE OF TITANIUM. **TITANOUS ACID,** Ti O_2 , may be obtained from *rutilite*, by fusing it in fine powder, in a platinum crucible, with thrice its weight of pure carbonate of potassa: a grey mass is obtained, which, after having been washed with water, is dissolved in hydrochloric acid, and on diluting with water, and boiling the solution, the greater part of the titanous acid is precipitated; it is collected, and washed with very dilute hydrochloric acid. In this state it still is apt to retain traces of iron and manganese, which may be separated by digesting the moist precipitate with hydrosulphuret of ammonia, which forms sulphurets with the iron and manganese, but does not affect the oxide of titanium: dilute hydrochloric acid removes the sulphurets, and the oxide of titanium, after being again washed, and heated red-hot, is pure. (ROSE, *Ann. Ch. et Ph.*, xxiii.)

Titaniferous Oxide of Iron, or *Titanate of Iron*, being more abundant than *rutilite*, is generally used as the source of titanous acid; it is pulverized, washed, and exposed at a high red-heat in a porcelain tube to the action of a current of dry sulphuretted hydrogen, as long as water is evolved: the oxide of iron is converted into sulphuret, but the titanous

acid undergoes no change: the product, when cold, is digested in hydrochloric acid, which leaves titanitic acid mixed with sulphur, from which it may be freed by heat; but as it still retains some iron, it must be again subjected to the action of the current of sulphuretted hydrogen in the porcelain tube; if afterwards treated by hydrochloric acid, well washed, and ignited, it is white and pure. (ROSE, *Ann. de Ph.*, LXXXVIII., and *Ann. Ch. et Ph.*, XXXVIII. 131.)

Titanic acid is white, very infusible, and very difficult of reduction: its sp. gr. is 3.93. Whenever it is heated it assumes a yellow color: when recently precipitated it dissolves in some of the acids, but becomes nearly insoluble after it has been ignited. (See H. ROSE, on the Modifications of Titanitic Acid. *Poggend.* LXI. 505, 531. *Chem. Gaz.*, Oct. 1844. *Ann. Ch. et Ph.*, Oct. 1844.) When its solution in hydrochloric acid is heated to the boiling-point, a part of the titanitic acid is always thrown down; but by slow evaporation to dryness, a soluble chloride remains. It is precipitated by the pure and carbonated alkalis; infusion of galls and ferrocyanide of potassium throw it down of a characteristic red color, and the precipitate is soluble in excess of the solution of the ferrocyanide. When a rod of zinc is immersed in its hydrochloric solution a purple precipitate (perhaps of the protoxide) is obtained. Recently precipitated titanitic acid is with difficulty separated from water upon a filter, but passes through in a milky state; the addition of a little acid or alkali facilitates its separation. It seems doubtful whether it forms any definite salts with the acids: but it unites with bases to form *titanates*. There are many resemblances between this oxide and the peroxide of tin. It consists of

							H. Rose.
Titanium.....	1	...	24	...	60	...	61
Oxygen	2	...	16	...	40	...	39
<hr/>							
Titanic acid	1		40		100		100

TITANIATE OF POTASSA. The peroxide of titanium may be united by fusion with several bases, forming a class of compounds which have been termed *Titanates*. When thus fused with potassa it yields a compound, from which water abstracts potassa, and leaves a white powder, composed of 18 potassa + 82 peroxide of titanium, and which is soluble in hydrochloric acid. (H. ROSE.)

BICHLORIDE OF TITANIUM, $TiCl_2$, is obtained by passing dry chlorine over metallic titanium, heated to redness. (GEORGE, *Ann. Phil.*, ix. 18.) It is a dense, transparent, and colorless fluid, fuming when exposed to air. It boils at a little below 212° , and acts violently upon water, evolving chlorine, and furnishing, when the water is not in excess, a white salt, very soluble, and deliquescent. The density of its vapor is, according to Dumas (*Ann. Ch. et Ph.*, XXXIII. 388), 6.836; and considering 1 volume of this vapor as composed of 1 volume of titanium vapor and 2 volumes of chlorine, he deduces the equivalent of titanium = 26.4. When this chloride is exposed to ammoniacal gas it absorbs it, and becomes solid, forming the compound from which Liebig, as above stated, obtained metallic titanium. It absorbs phosphuretted hydrogen, and forms a dry brown powder, which, when heated, yields a yellow subli-

mate, in which 3 atoms of the bichloride are combined with 1 of phosphuretted hydrogen. (ROSE.) It also forms crystallizable double salts with the alkaline chlorides. It consists of

						H. Rose.
Titanium	1	...	24	...	25	25.5
Chlorine	2	...	72	...	75	74.5
<hr/>						<hr/>
Bichloride of titanium	1		96		100	100.0

BIFLUORIDE OF TITANIUM. Ti F_2 . Titanic acid readily dissolves in hydrofluoric acid. When this solution is saturated with potassa and evaporated, a *titanofluoride of potassium* is the result, composed, according to Berzelius, of 1 atom of bifluoride of titanium + 1 atom of fluoride of potassium. Many other protoxides may be substituted for potassa; and hence the class of double salts which have been termed *titanofluorides*.

BISULPHURET OF TITANIUM, Ti S_2 , was obtained by Rose, by passing the vapor of sulphuret of carbon over ignited titanic acid. It has a dark-green or bronze color, and metallic lustre. It burns with a bluish flame into sulphurous and titanic acid; it is readily attacked by nitric and nitro-hydrochloric acid, and when boiled in solution of potassa or of soda, sulphurets and titaniates of the alkaline bases are formed. (*Quart. Jour.*, xvi. 97.) It is stated to consist of

Titanium	1	24	42.9
Sulphur	2	32	57.1
<hr/>					
Bisulphuret of titanium	1		56		100.0

SULPHATES OF TITANIUM. A white basic salt is precipitated on adding sulphuric acid to the diluted solution of titanic in hydrochloric acid. Sulphuric acid dissolves titanic acid even after the latter has been heated. When titanic acid is boiled in sulphuric acid diluted with half its weight of water, till the whole of the water is expelled, and then further heated, but not to redness, so as to drive off the excess of sulphuric acid, the residue, dissolved in water, furnishes an acid sulphate of titanium: this, if largely diluted and heated, or if alcohol be added to it, deposits the preceding basic sulphate. (H. ROSE. BERZELIUS.)

PHOSPHURET OF TITANIUM is formed, according to Chenevix, by heating the phosphate with charcoal and a little borax: it has a white metallic lustre, and is brittle.

PHOSPHITE OF TITANIUM is a white precipitate formed by adding ammonio-terchloride of phosphorus to the hydrochloric solution of titanic acid. (H. ROSE.)

PHOSPHATE OF TITANIUM falls when phosphoric acid is added to solution of peroxide of titanium in hydrochloric acid, in the form of a bulky white precipitate, which dries into a gummy mass. (H. ROSE.)

None of the other metals appear so to combine with titanium as to form true or definite alloys; but according to Berzelius, when it is blended with certain of them by fusion, it is susceptible of oxidizement, and consequently soluble in acids which otherwise do not act upon it.

CHARACTERS OF THE SALTS OF TITANIUM. Titanium is not thrown down in the metallic state by any other metal. The bulky red precipitate which its solutions afford with infusion of galls, is very characteristic; the other properties of its compounds will be evident from the preceding paragraphs. Before the blow-pipe, oxide of titanium becomes yellowish when ignited in a spoon, and upon charcoal dark-brown. With microcosmic salt it gives in the interior flame a fine violet-colored glass, more tending to blue than that from manganese. In the exterior flame this color disappears. With borax it gives a dirty hyacinth color. Titanic acid is sometimes used in enamel and porcelain painting as the source of a yellow color.

§ XXI. CERIUM. Ce. 46.

THE oxide of this metal, which is named after the planet Ceres, was obtained, in 1803, by Hisinger and Berzelius, from a mineral found at Bastnas in Sweden, to which they gave the name of *cerite*: it was originally, in consequence of its density, called *heavystone* (*schwerstein*), and was considered by Klaproth as containing a peculiar earth, which he termed *ochroit*. Oxide of cerium also occurs in *gadolinite*, and in several other minerals of Fahlun; and in *orthite*, which is not an uncommon ingredient of Scandinavian granite: it is also contained in *Allanite*, a mineral from Greenland.

Metallic cerium was first obtained by Vauquelin (*Ann. de Ch.*, iv.) and has subsequently been examined by Mosander and Beringer. Mosander obtained it by heating the dry chloride with potassium; violent action ensues, and a grey alloy of cerium and potassium results, which evolves hydrogen when put into water, and leaves the cerium in the form of a grey metallic powder, which, when dried and heated, burns brilliantly into an oxide, and is soluble in the weakest acids with the evolution of hydrogen. It very slowly acts upon water at common temperatures, but rapidly at a boiling heat, and the hydrogen thus evolved has a fetid odor. Heated in the air it burns into peroxide.

In consequence of Mosander's discovery of the uniform association of a large proportion of another metallic body with cerium, which he has termed *Lanthanum* (from *λανθάνειν*, to *lie concealed*), and of the usual presence of a second substance, but in much smaller quantity, to which he has given the name of *Didymium* (from *διδυμοι*, *twins*), much doubt arises as to the correctness of the descriptions usually given of the properties of cerium and its compounds. Beringer (*Ann. der Pharm.*, xlii. 134) has examined several of these freed from lanthanum, but there is so much resemblance between the combinations of these metals as to throw great difficulty in the way of an accurate account of their oxides and salts.

PROTOXIDE OF CERIUM. CeO . Cerite, which is a silicate of oxide of cerium, is the compound usually resorted to as a source of this oxide. The mineral is calcined, pulverized, and digested in hydrochloric acid: the solution evaporated to dryness and redissolved, leaves silica; the filtrate is accurately neutralized by ammonia, the iron thrown down by succinate of ammonia, and the filtered liquor then supersaturated by ammonia which throws down hydrated protoxide of cerium.

Berzelius obtains this oxide as follows: Cerite, calcined and pulverized, is boiled in nitrohydrochloric acid, and the solution evaporated to dryness. The residue, after having been gently heated, is dissolved in water, and the solution precipitated by benzoate of ammonia, which throws down the iron: the remaining solution is precipitated by caustic ammonia, and the precipitate (which is a mixture of the oxides of cerium) dissolved in hydrochloric acid, evaporated to dryness, and heated to redness in a retort as long as it evolves chlorine. The residuary salt is dissolved in water and precipitated by caustic potassa. This precipitate, which is *hydrated protoxide of cerium*, becomes yellow by exposure to air, and cannot be obtained free from water, for all attempts to dry it are attended by its partial peroxidizement. (See also *Remarks on Cerium* by Hermann, *Chem. Gaz.*, Jan., 1844) Protoxide of cerium consists of

						Hisinger.
Cerium	1	46	85.18 85.19
Oxygen	1	8	14.82 14.81
<hr/>						
Protoxide of cerium	1		54		100.00	100.00

But this oxide of cerium is blended, according to Mosander, with about 40 *per cent.* of oxide of lanthanum, together with some oxide of didymium, to separate which he dissolves in nitric acid, evaporates to dryness, heats the residue to redness, and digests it in a mixture of 1 part of nitric acid and from 50 to 100 of water, which dissolves the oxide of lanthanum and leaves the oxide of cerium nearly pure. According to Scheerer, it may be perfectly freed from all traces of lanthanum and didymium by solution in hydrochloric acid, neutralizing exactly by ammonia, adding acetate of ammonia, and then precipitating by oxalate of ammonia; the resulting oxalate of cerium collected upon a double filter, washed, dried, ignited, and again treated by the very dilute nitric acid, yields pure oxide of cerium.

[According to Mosander, the compounds of didymium are in many respects analogous to those of manganese: the oxide is brown; the sulphate amethystine: its oxide gives a brown color to oxide of cerium, and a red color to the salts of yttria.]

PROTOPEROXIDE OF CERIUM. YELLOW OXIDE OF CERIUM. (*Ceroxydoxidul* of Berzelius) is obtained by subjecting the peroxide of cerium at a red-heat to the action of hydrogen gas; or by subjecting the oxalate or carbonate of the protoxide of cerium to a white-heat. It is a lemon-yellow powder, soluble in hydrochloric acid with the evolution of chlorine, and which, when heated in the air, becomes peroxide. By dilute acids it is resolved into protoxide and peroxide. When free from lanthanum it appears according to Berzelius to be $CeO + 4[Ce_2O_3]$.

PEROXIDE OF CERIUM; SESQUIOXIDE OF CERIUM. Ce_2O_3 . When protonitrate of cerium is decomposed at a red-heat, or when protocarbonate of cerium is heated in the air, this oxide is generally obtained in the form of a reddish powder: but when free from oxide of didymium it is white. It is soluble in the acids, and when acted on by hydrochloric acid, it evolves chlorine: these solutions, when decomposed by potassa, afford a bulky precipitate of *hydrated peroxide of cerium*; it is pale-

yellow when moist, dark-yellow when dried. Ammonia generally throws down *subsalts* from these solutions. The moist hydrate is insoluble in the caustic alkalis. This oxide consists of

					Hisinger.
Cerium	2	...	92	...	79.31
Oxygen	3	...	24	...	20.69
<hr/>					
Peroxide of cerium	1		116		100.00

CHLORIDE OF CERIUM. $CeCl$. When the solution of the protoxide in hydrochloric acid is evaporated to dryness, a deliquescent *protochloride* is obtained, which is readily soluble in water and in alcohol; the latter solution burns with a green sparkling flame. The peroxide of cerium also dissolves in hydrochloric acid, but when it is gently heated, chlorine is evolved, and a protochloride formed. Chloride of cerium consists of

					Beringer.
Cerium	1	...	46	...	56.09
Chlorine	1	...	36	...	42.91
<hr/>					
Protochloride of cerium	1		82		100.00

IODIDE OF CERIUM. The solution of oxide of cerium in hydrochloric acid evolves iodine during evaporation, and leaves oxide of cerium after ignition.

BROMIDE OF CERIUM, $CeBr$, is uncrystallizable and very deliquescent: by heat it is converted into an *oxibromide*. (BERTHEMOT, *Ann. Ch. et Ph.*, XLIV. 393.)

BROMATE OF CERIUM. $CeO, BrO_5, 6HO$. When a hot saturated solution of protosulphate of cerium is precipitated by its equivalent of bromate of baryta, the filtrate, evaporated in vacuo over oil of vitriol, leaves foliated crystals, composed of

					Rammelsberg.
Protoxide of cerium	1	...	54	...	23.88
Bromic acid	1	...	118	...	52.24
Water	6	...	54	...	23.88
<hr/>					
Bromate of cerium	1		226		100.00

FLUORIDE OF CERIUM. CeF , is an insoluble yellow powder; it has been found *native* in the mines of Fahlun, in Sweden; and it exists in the mineral called *ytthrocerite*, combined with the fluorides of yttrium and of calcium. 100 parts of this mineral from Finbo contain 22 fluoride of cerium, 11 fluoride of yttrium, 67 fluoride of calcium.

SULPHURET OF CERIUM. CeS , may be obtained, according to Mosander, by passing the vapor of sulphuret of carbon over red-hot carbonate of cerium; or by fusing oxide of cerium with excess of sulphuret of potassium, and removing the soluble parts by washing with water. It is an orange-colored compound, and appears to consist of

					Mosander.
Cerium	1	...	46	...	74.19
Sulphur	1	...	16	...	25.81
<hr/>					
Sulphuret of cerium	1		62		100.00

SULPHITE OF CERIUM. Carbonate of cerium dissolved in aqueous sulphurous acid gave pale amethystine crystals. (KLAPROTH.)

HYPOSULPHATE OF CERIUM, formed by spontaneous evaporation of a solution of protocarbonate in hyposulphuric acid, crystallizes in delicate colorless prisms containing 42·79 of protoxide, 57·21 acid, *per cent.* (HEEREN.)

PROTOSULPHATE OF CERIUM. CeO,SO_3 , may be obtained by digesting the protocarbonate in dilute sulphuric acid: it yields small crystals, difficultly soluble in water: they become an anhydrous white powder when heated, composed of

						Rammelsberg.	Beringer.
Protoxide of cerium.....	1	54	57·45 57·306 57·442
Sulphuric acid	1	40	42·55 42·694 42·558
<hr/>							
Protosulphate of cerium	1		94		100·00	100·000	100·000

Otto has described two hydrated protosulphates: they form colorless crystals difficultly soluble in water, and are respectively $2[\text{CeO},\text{SO}_3] + 3\text{HO}$, and $\text{CeO},\text{SO}_3 + 3\text{HO}$.

PERSULPHATE OF CERIUM is a lemon-yellow salt, from which a red-heat expels half the acid, and converts it into a red *subpersulphate*. It is obtained by digesting peroxide of cerium in sulphuric acid diluted with 4 parts of water: it has an acid and sweetish taste. (HISINGER and BERZELIUS.)

PROTOSULPHATE OF CERIUM AND POTASSA. This double salt is obtained when solid sulphate of potassa is added to a solution of a proto-salt of cerium: as it dissolves, a white powder falls, which is the potassa-sulphate of cerium, and in this way, by using excess of sulphate of potassa, the whole of the cerium is thrown down: the double salt, though soluble in water, is insoluble in solution of sulphate of potassa. It is deposited from its solution in boiling water in small crystals of a pale amethyst color. At a red-heat it fuses, but is not decomposed: the alkalis throw down a basic salt from its solution, which can only be perfectly decomposed by long digestion in excess of alkali. This is the most characteristic salt of cerium, and it serves to separate the oxide of cerium, in analytical operations. (BERZELIUS.) There is also a persulphate of cerium and potassa.

PROTOSULPHATE OF CERIUM AND SODA. A saturated solution of sulphate of soda added to protosulphate of cerium precipitates this double salt, and at a boiling-heat the whole of the oxide of cerium is thus separated. A crystal of sulphate of soda suspended in a solution of sulphate of cerium produces a similar precipitation. (BERINGER.) It consists of

							Beringer.
Soda	1	32	12·32	12·694
Protoxide of cerium	2	108	41·53	41·248
Sulphuric acid	3	120	46·15	46·058
<hr/>							
Soda-sulphate of cerium	1		260		100·00		100·000

PHOSPHURET OF CERIUM was obtained by Mosander by heating cerium with phosphorus; and, in the form of a grey powder, by passing phosphuretted hydrogen gas over oxide of cerium at a white heat.

PROTOPHOSPHATE OF CERIUM is an infusible white powder, soluble in hydrochloric and nitric acids, but insoluble in excess of phosphoric acid. It occurs *native*.

CARBURET OF CERIUM is obtained, according to Mosander, by heating the oxalate in a retort: a mixture of peroxide and of carburet remains, which when digested in hydrochloric acid leaves the pure carburet: it is dark-brown, heavy, and insoluble in the acids: heated in the air it burns into peroxide.

PROTOCOLCARBONATE OF CERIUM. CeO,CO_2 , is precipitated by the carbonated alkalis, in the form of a white powder, insoluble in water and in excess of carbonic acid. It is decomposed by a strong heat, and if exposed to air, peroxide of cerium remains, but if air be excluded, the proto-peroxide (*oxyd-oxydul*) is formed. (HISINGER and BERZELIUS.) It has been found *native*. When protoxide of cerium is exposed to air it gradually absorbs carbonic acid. When the protosalts of cerium are decomposed by carbonate of ammonia the carbonate first falls as a flocculent white precipitate, which, if left in the liquid, gradually becomes crystalline; it is insoluble in water, and in aqueous carbonic acid, and consists of

						Beringer.
Protoxide of cerium.....	1	54	52.43 53.31
Carbonic acid	1	22	21.36 21.91
Water	3	27	26.21 24.78
<hr/>						
Hydrated protocarbonate of cerium	1		103		100.00	100.00

PERCARBONATE OF CERIUM. $C_2O_3,3CO_2$, much resembles the protocarbonate in appearance, but it is heavier and of a less pure white color, and soluble in water: it consists of

						Hisinger.
Peroxide of cerium.....	1	116	63.74 63.83
Carbonic acid	3	66	36.26 36.17
<hr/>						
Carbonate of peroxide of cerium	1		182		100.00	100.00

CHARACTERS OF THE SALTS OF CERIUM. The *protosalts* of cerium, when pure, are colorless, but from the presence of a trace of cobalt or manganese, or probably of didymium, they often acquire a pink hue: they are of a sweet and astringent taste, and bear much general resemblance to the salts of yttrium. With ammonia and potassa they give white hydrated oxide insoluble in excess of those alkalis: the carbonate of cerium thrown down by carbonates of alkalis, is to a small extent soluble in excess of the precipitants. Phosphate of soda throws down phosphate of cerium soluble in nitric acid; a strong solution of sulphate of potassa throws down the double sulphate above mentioned. Oxalic acid and the oxalates throw down oxalate of cerium, only soluble in excess of hydrochloric and nitric acids. These salts are unaltered by infusion of galls and by sulphuretted hydrogen, but are precipitated by the

hydrosulphuretted alkalis. Ferrocyanide of potassium occasions in them a white precipitate. The salts of the *peroxide* are of a yellow color, and the hydrosulphurets occasion in them a white precipitate: they are precipitated as above stated by sulphate of potassa. Boiled with hydrochloric acid, chlorine is evolved, and they become protosalts. None of the other metals precipitate cerium in a metallic state.

Before the blow-pipe the oxide of cerium becomes red-brown when ignited. When the proportion is small, it forms with the fluxes a clear, colorless glass, which by increasing the proportion of oxide becomes yellowish-green while hot. With microcosmic salt, if heated a long time in the internal flame, it gives a clear colorless glass. With borax under similar circumstances, it gives a faint yellow-green glass while warm, but is colorless when cold. Exposed again for some time to the external flame, it becomes reddish-yellow, which color it partly retains when cold. If two transparent beads, one of the compound with microcosmic salt, the other with borax, be fused together, the compound becomes opaque and white.

§ XXII. LANTANUM. La. 40.

It has been stated in the preceding section that the minerals containing cerium, contain also another metal, which, as it had hitherto lain concealed in oxide of cerium, was called *Lanthanum*. To separate the oxides of these metals their mixture is dissolved in nitric acid, evaporated to dryness, and the residue exposed to a red-heat; it is then digested in very dilute nitric acid (1 of acid to 100 of water), which dissolves the oxide of lanthanum and leaves that of cerium; the former may be thrown down in the form of a carbonate by a carbonated alkali; when ignited it acquires a dirty red hue, and in hot water becomes a white hydrate; it dissolves in a solution of hydrochlorate of ammonia with the gradual expulsion of ammonia. The salts of the oxide of lanthanum are astringent, but not sweet; their crystals generally have a reddish tint, and their solutions, when free from cerium, are not precipitated by the addition of sulphate of potassa. According to Mosander the salts of lanthanum are colorless, and derive their red or amethystine tint from the presence of *didymium*. (On the separation of lanthanum and the properties and composition of its salts, see HERMANN. *Chem. Gaz.*, Feb. 1844. MOSANDER. *Ann. Ch. et Ph.*, xi. 469.) By acting upon dry chloride of lanthanum by sodium, Mosander obtained metallic lanthanum in the form of a dark lead-colored powder, slowly acted on by air and cold water, and forming a mucilaginous hydrated oxide. The atomic weight of lanthanum has not been accurately determined, but it appears to be certainly below that of cerium. Rammelsberg places it at about 44; Choubine and Otto at 36. The mean of the few analyses of its compounds hitherto made, would indicate its equivalent as about = 40.

§ XXIII. TELLURIUM. Te. 64.

In the year 1782, Müller von Reichenstein showed that certain Transylvanian gold ores contained a new and distinct metal, and his experiments were verified by Klaproth in 1798, who named this new metal *Tellurium* (from *tellus*, the earth).

The ores of tellurium are, 1. *Native*; in which the metal is combined with iron and a little gold. 2. *Graphic ore*; which consists of tellurium, gold, and silver. 3. *Yellow ore*; a compound of tellurium, gold, lead, and silver; and 4. *Black ore*; consisting of the same metals with copper and sulphur. 5. *Bismuthic Tellurium*. These ores have been found in the Transylvanian mines, in Siberia, and in Hungary. Sulphuret of bismuth and tellurium, (analysed by Damour,) has been found in Brazil. (*Ann. Ch. et Ph.*, Mars, 1845.)

Klaproth obtained tellurium from the auriferous native ore, by dissolving in nitrohydrochloric acid, diluting the solution with water, but not so as to occasion a precipitate, supersaturating with potassa, filtering (from gold and peroxide of iron), and neutralising by hydrochloric acid, which throws down oxide of tellurium; this is washed, dried, and reduced in a retort by heating it with about a tenth part of charcoal; the reduced tellurium is partly found at the bottom of the retort, and a part of it sublimes. Berzelius has given several processes for obtaining the metal from the argentiferous (or graphic) ore, which usually contains about 35 *per cent.* of tellurium, and from 50 to 60 *per cent.* of silver, the remainder being gold; and from the bismuthic ore, the average composition of which is 60 *per cent.* of bismuth, 36 of tellurium, and 4 of sulphur: it also often contains silver and selenium. He treats the latter as follows: it is triturated and washed with water to separate the earthy from the metallic parts: the metallic powder is mixed with its weight of carbonate of potassa or soda and olive oil, and this paste is carefully heated in a covered porcelain crucible, so as to carbonise the oil; the heat is then gradually raised to whiteness, by which a brown porous mass is produced, which is a mixture of carbon with an alloy of bismuth, tellurium, and potassium; this is washed upon a filter with water which has been deprived of air by boiling, and all access of air as far as possible excluded; air is then blown through the red filtered liquor, to precipitate the tellurium, which is washed and fused, and freed by distillation from gold, iron, copper, and manganese, which remain as the residue, still retaining a little tellurium; the distillation of the tellurium is much facilitated by passing a current of hydrogen gas through the apparatus. For other processes see BERZELIUS' *Lehrbuch*.

Tellurium is of a bright tin color, brittle, fusible at a temperature a little above melting lead, volatile at a red-heat, when it forms a yellow vapor. Its specific gravity is 6.1 to 6.3. Its specific heat, as determined by Regnault, is 0.05155. It is easily crystallizable; and, for a metal it appears to be a bad conductor of heat and electricity; indeed, it may be said, in some respects, to form a kind of connecting link between sulphur or selenium and the metals, as far as its general habitudes are concerned. The equivalent of tellurium may be assumed as 64. (64 GMELIN. 64.2 BERZELIUS.)

OXIDE OF TELLURIUM. No *protoxide* of tellurium = TeO , has as yet been obtained.

BINOXIDE OF TELLURIUM. TELLUROUS ACID. TeO_2 . Exposed to heat and air, tellurium burns, exhaling a peculiar odor, (which Berzelius ascribes to selenium,) and forming a white oxide. This oxide is also

obtained by evaporating the nitrate to dryness, and exposing the residue to a dull-red heat. It is also deposited in minute crystals, when a hot solution of bichloride of tellurium is mixed with boiling water, and the whole allowed to cool slowly. It becomes yellow when heated, and fuses at a red-heat, concreting into a crystalline mass on cooling: it sublimes at a white-heat: it consists of

						Berzelius.	Klaproth.
Tellurium	1	...	64	...	80 80.11 83.14
Oxygen	2	...	16	...	20 19.89 16.86
<hr/>							
Tellurous acid	1		80		100	100.00	100.00

Hydrated tellurous acid is thrown down on diluting the solution of this oxide in nitric acid, sp. gr. 1.25; or by decomposing tellurite of potassa by nitric acid: it forms a bulky flocculent precipitate of a metallic taste, reddening litmus, and soluble in water; but when this solution is heated to about 110° , it becomes milky, and deposits anhydrous tellurous acid in the form of a crystalline precipitate.

In its anhydrous state this oxide of tellurium is difficultly soluble, but when hydrated it readily dissolves in most of the acids, forming colorless solutions of a nauseous metallic taste, which according to Kölreuter are powerfully emetic: they afford metallic tellurium when acted on by phosphorus, and also by sulphurous acid, and by zinc, iron, tin, lead, copper, and some other metals: most of the solutions of this oxide in the mineral acids are decomposed by copious dilution with water, provided there be no great excess of acid; with the alkalis and their carbonates they give precipitates of hydrated oxide soluble in excess of the precipitant, especially when aided by heat: they are precipitated white by phosphate of soda; dark-brown by sulphuretted hydrogen and alkaline hydrosulphurets; and yellow by tincture of galls: they are not affected by ferrocyanide of potassium, nor by oxalic acid.

The basic combinations of tellurous acid, or *tellurites*, are obtained by dissolving the hydrated acid in the alkalis; or by double decomposition; or by fusion: the alkaline tellurites are soluble in water: those of baryta, lime, and strontia are difficultly soluble; and most of the other compounds insoluble in water: they are nearly all readily soluble in hydrochloric acid.

PEROXIDE OF TELLURIUM. **TELLURIC ACID**, TeO_3 , may be obtained by passing chlorine through the solution of tellurous acid in excess of potassa till it is fully saturated, and the first precipitate entirely redissolved; a little chloride of barium is then added to separate any accidental traces of sulphuric or of selenic acids, and the filtrated liquor is neutralized by ammonia, and chloride of barium added, which occasions a precipitate of *tellurate of baryta*; this, digested with a fourth of its weight of sulphuric acid (diluted with water), yields a solution, which, when filtered and carefully evaporated, affords crystallized *hydrated telluric acid* = $\text{TeO}_3, 3\text{HO}$, from which adhering sulphuric acid may be removed by alcohol. This hydrate loses its water by heat, and the *anhydrous acid*, of a lemon-yellow color, remains, constituted, according to Berzelius, of

						Berzelius.	
Tellurium	1	...	64	...	72.73	...	72.77
Oxygen	3	...	24	...	27.27	...	27.23
<hr/>							
Telluric acid	1		88		100.00		100.00

Anhydrous telluric acid is insoluble in water: the crystallized acid dissolves slowly but abundantly in water at 65° , and is rapidly soluble to any extent in boiling water. Dried at 320° , the crystals lose 2 atoms of water, and become anhydrous at a temperature a little below redness: they are insoluble in absolute alcohol.

The *tellurates* have been almost exclusively examined by Berzelius: those of the alkalis are moderately soluble in water; those of the alkaline earths very sparingly soluble; and many of the other tellurates are insoluble. The soluble tellurates give bulky precipitates with chloride of barium, which afterwards become granular: they are soluble in hydrochloric and nitric acids.

TELLURIUM AND CHLORINE. When tellurium is gently heated in chlorine it burns, forming a dark liquid, which by the action of excess of chlorine becomes yellow, and concretes on cooling into a white and extremely deliquescent crystalline mass $= \text{TeCl}_2$. If this be heated with pulverised tellurium, a dark purple protochloride is formed $= \text{TeCl}$, more volatile than the bichloride, and giving a vapor resembling that of iodine.

TELLURIUM AND IODINE. 64 parts of pulverised tellurium gently heated with rather more than 126 of iodine, yield a dark flocculent sublimate of insoluble protiodide of tellurium $= \text{TeI}$. When hydrated tellurous acid is digested in aqueous hydriodic acid, a black granular compound $= \text{TeI}_2$ is obtained, which when heated loses iodine, and becomes TeI . Water resolves it into a tellurite of the biniodide, and hydriodic acid: $3\text{TeI}_2 + 4\text{HO} = \text{TeI}_2, 2\text{TeO}_2 + 4\text{HI}$.

TELLURIUM AND BROMINE. When bromine is heated with excess of tellurium a purple vapor rises, which condenses in black acicular crystals $= \text{TeBr}$. When powdered tellurium is added to excess of bromine in a tube cooled by ice, a fusible orange-colored crystalline substance is obtained $= \text{TeBr}_2$.

TELLURIUM AND HYDROGEN. When tellurium is negatively electrized in contact with water, a brown powder is produced, which has been described as a solid *hydruret*, but which, according to Magnus, is only finely-divided tellurium. When an alloy of tellurium and tin is acted on by hydrochloric acid, *telluretted hydrogen gas* is evolved; it reddens litmus, dissolves in water, and possesses the general habitudes of sulphuretted hydrogen. According to Bineau, (*Ann. Ch. et Ph.*, lxxviii. 424,) the sp. gr. of telluretted hydrogen gas is 4.489; and it probably consists of

Tellurium	1	...	64	...	98.46
Hydrogen	1	...	1	...	1.54
<hr/>					
Telluretted hydrogen gas	1		65		100.00

SULPHURETS OF TELLURIUM. There appear to be two sulphurets of tellurium, which, according to Berzelius, act as *sulphur acids*; they are obtained by the decomposition of tellurous and telluric acids by sulphuretted hydrogen.

THE SALTS OF TELLURIUM are decomposed by the alkalis, and the precipitate is redissolved when they are added in excess. Hydrosulphuret of ammonia forms a brown precipitate; ferrocyanide of potassium occasions no change. Zinc, lead, tin, copper, cadmium, or iron, immersed into the solutions, cause the separation of metallic tellurium; it generally appears as a black powder, which acquires lustre by friction.

The oxides (or acids) of tellurium combine with many of the oxides of the heavy metals, and produce a class of metallic *tellurites* and *tellurates*: as these have hitherto been almost exclusively examined by Berzelius, I must refer for details to his papers in Poggendorff's *Journal*, and to the abstracts given in his *Lehrbuch*, and in Gmelin's *Handbuch*. Nearly all our information respecting this singular and rare metal is indeed derived from the same indefatigable authority.

§ XXIV. ARSENIC. As. 75.

THE distinct metallic characters of this substance were first noticed by Brandt, in 1773; but it was probably known to Paracelsus, and a process for obtaining it is given by Schroeder, in his *Pharmacopœia*, published in 1649. Its general chemical relations are such as to place it rather among the simple acidifiable substances than among the metals, for it forms no salifiable base with oxygen, but constitutes *acids*: it, however, has the lustre and opacity of a metal, and conducts electricity. It occurs *native*, and in the form of *native oxide*; and there are many *native arseniates*: it also occurs as a *sulphuret*; and is frequently found in combination with other sulphurets, especially with sulphuret of iron, constituting *arsenical pyrites* = $\text{Fe}_2\text{As}_2\text{S}_2$. During the roasting of the arseniferous sulphurets of copper, iron, cobalt, and nickel, large quantities of oxide of arsenic are formed, and from such sources the commercial demands are supplied. Traces of arsenic are found in several other minerals, and consequently in several of their products, as in sulphur and sulphuric acid, in zinc, in sulphuret of antimony, and occasionally in phosphorus. Orfila once suspected the presence of arsenic in bone, and some of the animal tissues, but afterwards found he was in error. (*Ann. Ch. et Ph.*, LXXvii. 159.)

Arsenic may be obtained from the purified *white arsenic* of commerce, by mixing it with its weight of *black flux*, and introducing the mixture into a Florence flask or small retort, placed in a sand-bath, gradually raised to a red-heat: a brilliant metallic sublimate of pure arsenic collects in the upper part of the flask or in the neck of the retort. The volatility of white arsenic prevents its easy reduction by charcoal alone; but the potassa in the flux enables it to acquire a temperature sufficient for its perfect reduction. Arsenic may also be obtained by heating the ore called *native arsenic* (*scherbenkobalt* of the Germans) in coarse powder in a retort; the metal sublimes, leaving the impurities behind.

Arsenic is of a steel-grey color, crystalline texture, quite brittle, and of a specific gravity = 5.7 to 5.9. Its specific heat, as ascertained by Regnault, is 0.08140. It volatilizes, and in close vessels may be sublimed at a temperature lower than its fusing-point: this is generally stated to be about 360° , but according to Fischer it does not rise in vapor below a dull red-heat, and about that required for the fusing of zinc: indeed the

attempts to fuse arsenic seem not to have succeeded; and when it has been heated for this purpose in sealed glass tubes, the tension of its vapor has burst the tube, but the metal has not melted. The density of arsenic vapor is about 10·37: it has a characteristic alliaceous odor. The atomic weight of arsenic is 75. (75 GMELIN. 75·34 GRAHAM. 37·67 BERZELIUS. TURNER.)

Native Arsenic has been found in Saxony, Hanover, France, Bohemia, and Cornwall. It usually occurs in rounded masses, or nodules, of a foliated lamellar texture, in the veins of primitive rocks, and is often associated with silver, cobalt, lead, and nickel ores. Its color in the fresh fracture is nearly tin-white, but it speedily tarnishes, and becomes greyish black.

ARSENIC AND OXYGEN. There are three compounds of arsenic and oxygen, namely, a suboxide, arsenious acid, and arsenic acid: the first is not salifiable, and the two latter can scarcely be said to form definite salts with any of the stronger acids, but they both unite with bases forming *arsenites* and *arseniates*.

PROTOXIDE OF ARSENIC. SUBOXIDE OF ARSENIC. AsO . When metallic arsenic is exposed to damp air, it gradually crumbles into a grey powder, which appears to contain between 9 and 10 *per cent.* of oxygen. Some samples of arsenic undergo this change more rapidly than others, which has been ascribed to the presence of potassium, the metal having been reduced by a flux containing potassa. When heated out of contact of air, this oxide is resolved into arsenious acid, which sublimes, leaving metallic arsenic.

ARSENIOUS ACID. WHITE ARSENIC. WHITE OXIDE OF ARSENIC. AsO_3 . This is the best known, and most commonly occurring compound of arsenic. It is formed by the combustion of the metal; but it is generally obtained by the joint action of heat and air on certain arseniferous ores. It is abundantly prepared at Joachimsthal in Bohemia, from arsenical pyrites and arsenical cobalt, which are roasted in reverberatory furnaces, and the vapors condensed in a long flue, or series of chambers, the contents of which, submitted to a second sublimation, afford the *white arsenic* of commerce.

Arsenious acid generally occurs in white translucent vitreous masses, often of a slight buff tint, and occasionally transparent, especially when first removed from the subliming vessel: on breaking the more opaque pieces, a transparent glassy nucleus is often found within them. When slowly sublimed in a current of air, as in a tube open at both ends, the vapor condenses in regular octohedral crystals; but if rapidly sublimed, it forms a white powder, which, however, under the microscope, is evidently crystalline. The massive arsenious acid of commerce is generally pure, but when purchased in powder, it is sometimes adulterated. To obtain it perfectly pure, the vitreous acid of commerce should be finely powdered and digested for some hours in aqueous solution of ammonia at 160° or 170° , frequently shaking the vessel: the clear warm solution is then poured off, and on cooling it deposits octohedral crystals of the acid, pure and free from ammonia. (BERZELIUS.) Wöhler has observed that the acid occasionally crystallizes in hexahedral plates derived from a rhombic

prism, (*Ann. Ch. et Ph.*, Li. 201,) so that it appears to be dimorphous, and this dimorphism seems connected with the peculiarities of the opaque and vitreous state of the fused acid. The temperature at which arsenious acid rises in vapor is below that at which it fuses, and appears to be about 425° . The density of its vapor is 13.85, (MITSCHERLICH,) and it is inodorous. When heated under pressure, or when suddenly and highly heated, it fuses, and concretes on cooling into a transparent glass. Arsenious acid is sometimes described as insipid, and some have represented it as acrid and acid. When the tongue is applied to the vitreous acid, it at first seems nearly tasteless, afterwards slightly acid, sweet, and astringent.

The specific gravity of the opaque white arsenious acid is about 3.6, (3.529, TAYLOR; 3.69, GUIBOURT): that of the transparent vitreous and fused acid is about 3.7 (3.698, DUMAS; 3.70, KARSTEN; 3.738, GUIBOURT; 3.798, TAYLOR.) The transition of the vitreous into the opaque, or of the amorphous into the crystalline acid, is accelerated by elevation of temperature, and is independent of the presence of air or moisture: according to Christison, it may be preserved in its vitreous state under water and in alcohol. The solubility of arsenious acid in water has been variously stated, and appears in some measure dependent upon its isomeric modifications. Guibourt found that 100 parts of water at 60° dissolved 0.96 of the vitreous, and 1.25 of the opaque acid; and that at 212° , 9.68 of the former and 11.47 of the latter were dissolved; and that when these solutions had cooled down to 60° , 1.78 of the vitreous and 2.9 of the opaque were retained. The solution of the vitreous acid reddened litmus, but that of the opaque acid not only did not redden litmus, but exhibited a slight alkaline reaction. When ammonia is poured upon the powder of the vitreous acid, a slight degree of heat is evolved, and it at the same time acquires the properties of the opaque modification. When a concentrated solution of the vitreous acid in boiling hydrochloric acid is suffered to cool, the crystals which it deposits have the properties of the opaque acid, and this transition from the one modification to the other is attended by the evolution of light (p. 122); but if the milky acid be used, or if the deposited crystals be re-dissolved, the crystals which are then deposited from the hydrochloric solution are formed without any luminous appearance. (H. ROSE.) Arsenious acid consists of

					Mitscherlich.		Berzelius.		Davy.		
Arsenic	1	75	75.76	75.73	75.782	75
Oxygen	3	24	24.24	24.27	24.218	25
<hr/>											
Arsenious acid	1		99		100.00		100.00		100.000		100

Arsenious acid is decomposed at a dull red-heat by hydrogen, and by carbon and many of the metals. The aqueous solution of arsenious acid is rendered yellow by aqueous sulphuretted hydrogen, and when the solution is acidulated by hydrochloric acid, a yellow precipitate of tersulphuret of arsenic falls; $\text{AsO}_3 + 3\text{HS} = \text{AsS}_3 + 3\text{HO}$: the yellow tint is observed when a 10,000th of arsenious acid is present, and the yellow precipitate is visible in an acidulated solution of 1 part of arsenious acid in 80,000 of water. (LASSAIGNE.) Excess of lime water occasions a white precipitate in water containing about one-500th of arsenious acid.

Ammoniacal solution of oxide of copper gives an apple-green precipitate in solution of arsenious acid, thus indicating about a 12,000th part of the acid. When a slip of bright copper leaf is boiled in an aqueous solution of arsenious acid acidulated by hydrochloric acid, a grey film of arsenic is deposited upon the copper: this test will indicate the presence of less than a 100,000th part of arsenious acid. (REINSCH.) With nitrate of silver the arsenious acid gives a yellow precipitate.

Traces of arsenious acid are not unfrequent in various chemical and pharmaceutical preparations: it has been detected in sulphuric, hydrochloric, and phosphoric acids, in phosphate of soda, and in emetic tartar. Berzelius observes that he has never found a sample of the latter salt which did not exhale a very perceptible arsenical odor when heated by the blow-pipe.

This acid is used in many of the arts, especially in color-making, dyeing and calico-printing, and in the manufacture of stearine candles; is also used in medicine, and in a variety of preparations for the destruction of vermin: it is virulently poisonous, producing a set of peculiar symptoms, ultimately followed by inflammation and gangrene of the stomach and intestines: it also proves fatal when applied to a wound; and as the local injury is not sufficient to cause death, it is probable that an induced affection of the nervous system and of the heart is the immediate cause of the mischief. (BRODIE'S *Observations and Experiments on the Action of Poisons*, *Phil. Trans.*, 1812, p. 209.) To get rid of the poison by producing copious vomiting and purging, and to pursue the usual means for subduing and preventing inflammation, are the principal points of treatment to be adopted in cases where this substance has been taken. (ORFILA, *Traité des Poisons*, i. 123. CHRISTISON, *on Poisons*. TAYLOR, *Med. Jurisp.*) Several antidotes have been proposed in such cases, but none have proved efficient: the moist and recently-precipitated hydrated peroxide of iron, and a saturated solution of it, in acetic acid, are said in some cases to have subdued the most alarming symptoms.

COMBINATIONS OF ARSENIOUS ACID WITH BASES. ARSENITES. These salts, when heated, either evolve arsenious acid or metallic arsenic: in the latter case they are converted into *arseniates*; thus, $5[\text{KO}, \text{AsO}_3] = 3[\text{KO}, \text{AsO}_5] + 2\text{As}$: heated with charcoal metallic arsenic sublimes. The alkaline arsenites, when in solution, are decomposed by lime and the salts of lime, and a white precipitate of *arsenite of lime* falls: they are precipitated green by solutions of copper, and yellow by nitrate of silver. They are not precipitated by sulphuretted hydrogen, except excess of a stronger acid be present: in this way the hydrochloric solutions of those arsenites which are insoluble in water may also be decomposed. When metallic arsenic is heated with hydrate of potassa, hydrogen gas is evolved, and arsenuret of potassium and arsenite of potassa are formed; the potassa, therefore, and the water, are both decomposed; if the heat be raised to redness, the arsenious acid is resolved into metallic arsenic and arsenic acid: with hydrate of soda the phenomena are similar; with hydrate of lime and baryta no arsenic acid is produced. (SOUBEIRAN *Ann. Ch. et Ph.*, xliii.)

The *arsenites of ammonia, potassa, and soda*, are easily soluble and uncrystallizable: they are formed by dissolving the acid in the alkaline

solutions. Berzelius has shown that the supposed crystals of arsenite of ammonia deposited by the solution of arsenious acid in ammonia, are quite destitute of ammonia, and consist only of arsenious acid. When arsenious acid is dissolved in the alkaline carbonates, it is deposited unaltered by evaporating the solution, so that it is doubtful whether this acid expels carbonic acid, in the humid way. The *arsenites* of *lime*, *buryta*, *strontia*, and *magnesia*, are difficultly soluble in water, but readily soluble in hydrochloric acid: there are two arsenites of lime, one basic $=2\text{CaO}, \text{AsO}_3$; the other neutral, CaO, AsO_3 . (SIMON, *Poggend.*, XL. 417.) *Arsenite of potassa* is the active ingredient in the *liquor arsenicalis* of the *Pharmacopœia*, and in *Fowler's mineral solution* or *tasteless ague-drop*. It produces a white precipitate in the protosalts of manganese, a dingy-green precipitate in the solutions of iron, a white precipitate in solutions of zinc and tin. Mixed with a solution of sulphate of copper, a precipitate of an apple-green color falls (*Scheele's green*), used as a pigment: it is prepared by dissolving 2 parts of sulphate of copper in 44 of hot water, and gradually adding it to a solution of 2 parts of carbonate of potassa and 1 of arsenious acid in 44 of hot water, the whole being well stirred during mixture; the arsenite of copper, in the form of a fine green powder, is gradually deposited, and is to be washed and dried at 212° . A similar preparation, known under the name of *Schweinfurth green*, is made as follows: 50 lbs. of sulphate of copper and 10 of lime are dissolved in 20 gallons of vinegar, and a boiling-hot solution of 50 lbs. of arsenious acid quickly stirred into it; the precipitate is dried and reduced to a fine powder. In the solutions of lead, antimony, and bismuth, arsenite of potassa forms white precipitates: added to nitrate of cobalt, it forms a pink precipitate; and bright yellow, with nitrate of uranium. With nitrate of silver it forms a white precipitate, soon becoming yellow, and very soluble in ammonia. All these precipitates are probably *arsenites* of the respective metals, and, heated by a blow-pipe on charcoal, they exhale the smell of arsenic. They are decomposed when boiled in solution of carbonate of potassa or of soda: they are mostly soluble in excess of arsenious acid, and easily soluble in nitric acid, and in such other acids as form soluble compounds with their bases.

Native Arsenite of Lead is found in France, in Spain, and in Siberia.

ARSENIC ACID, AsO_5 , was discovered by Scheele; it is obtained by distilling a mixture of 1 part of hydrochloric and 12 of nitric acid off 4 parts of arsenious acid; nitric oxide gas is given off, and when the contents of the retort have acquired the consistence of thin syrup, they are poured into a porcelain dish, and evaporated by a moderate heat: suddenly, the arsenic acid (which is anhydrous) concretes into an opaque white mass, which should be put, whilst warm, into a well-stopped phial. The hydrochloric acid is only useful in promoting the solution of the white arsenic, which otherwise adheres to the retort, and occasions irregular ebullition. Arsenic acid may also be procured by distilling nitric acid off powdered metallic arsenic.

Arsenic acid is deliquescent, and uncrystallizable: it fuses at a heat approaching to redness, and concretes on cooling into a vitreous mass; at a higher temperature it is decomposed, oxygen is evolved, and arsenious

acid sublimes. Its specific gravity is about 3·7. It requires for solution 6 parts of cold and 2 of boiling water; its solution reddens vegetable blues, tastes acid and metallic, and is a virulent poison. When water is poured upon the solid acid, part only is immediately dissolved, and another portion, as is the case with phosphoric acid, remains undissolved, but after a time, upon agitating the solution, the whole is taken up. If the dry acid be exposed to air, so as gradually to deliquesce, it sometimes forms crystals which are extremely soluble, and are probably *hydrated acid*. Arsenic acid gives a white precipitate with lime-water, and a peculiar reddish-brown with nitrate of silver; it gradually yields a yellow deposit of a sulphuret of arsenic when its solution is subjected to the continuous action of a current of sulphuretted hydrogen gas; its precipitate with ammoniacal oxide of copper is pale greenish-blue. It consists of

					Proust.	Mitscherlich.	Berzelius.	Thenard.					
Arsenic.....	1	...	75	...	65·22	...	65	...	65·04	...	65·283	...	65·4
Oxygen.....	5	...	40	...	34·78	...	35	...	34·96	...	34·717	...	34·6
<hr/>													
Arsenic acid	1		115		100·0		100		100·00		100·000		100·0

ARSENIATES are produced by the union of this acid with the metallic oxides; and many which are insoluble may be formed by adding arseniate of potassa to their respective solutions. The normal arseniates are constituted like the phosphates, of 1 atom of acid with 3 of base, and there are also salts with 2 and 1 of basic oxide, in which the deficient base is replaced by 1 and 2 atoms of water; but there appear to be no modifications corresponding to the pyrophosphates and metaphosphates. (GRAHAM.) The arseniates which are insoluble in water are soluble in dilute nitric acid, and in such other acids as do not form insoluble compounds with their bases, and ammonia precipitates them from these solutions. They are readily decomposed by charcoal at a red-heat; but many of them, when heated alone, are unchanged even at a higher temperature. They are decomposed when boiled in solutions of the fixed alkaline carbonates. The soluble arseniates generally give a white precipitate with lime water: they are not immediately precipitated by solution of sulphuretted hydrogen: protosulphate of iron gives a white precipitate (or yellowish if arsenious acid be at the same time present.) With solutions of lead and of zinc they give white precipitates; yellow with the persalts of uranium and mercury; red with the solutions of salts of cobalt; green with those of nickel; pale greenish-blue with those of copper; and reddish-brown with those of silver. These precipitates are mostly soluble in hydrochloric acid, and in solutions of ammoniacal salts. Arseniate of potassa gives a yellow precipitate with persulphate of uranium when the solution is so diluted as to contain only a 10,000th part of arsenic acid, and with protosulphate of iron a white cloud is perceptible under the same state of dilution. All the arseniates, when dissolved in water or in dilute nitric acid, give a white precipitate with acetate of lead, which fuses and emits arsenical fumes when heated on charcoal before the blow-pipe.

ARSENIATES OF AMMONIA. When ammonia is added to a concentrated solution of arsenic acid till a precipitate ensues, and this is re-dissolved by heat, the liquor gradually forms prismatic efflorescent crystals resem-

bling the corresponding phosphate of ammonia: they are bibasic, and may be represented as $=2\text{NH}_4\text{O},\text{HO},\text{AsO}_5$. When ammonia is added to a concentrated solution of this salt, a difficultly-soluble compound is formed $=3\text{NH}_4\text{O},\text{AsO}_5$: exposed to the air, it reverts by loss of ammonia to the bibasic salt. When ammonia is supersaturated with arsenic acid and the solution evaporated, large crystals are obtained, exactly resembling those of the corresponding phosphate, $=\text{NH}_4\text{O},2\text{HO},\text{AsO}_5$: they are very soluble and deliquescent. (MITSCHERLICH.)

ARSENIATES OF POTASSA. The tribasic arseniate, $3\text{KO},\text{AsO}_5$, is deposited in small deliquescent acicular crystals, on evaporating a solution of arsenic acid supersaturated by potassa. (GRAHAM.) The same salt is produced by fusing the bibasic arseniate with carbonate of potassa, when 1 atom of carbonic acid is expelled. (MITSCHERLICH.) When carbonate of potassa is added to aqueous arsenic acid, as long as effervescence ensues, an alkaline salt is obtained on evaporation, which becomes vitreous when heated, and is $=2\text{KO},\text{AsO}_5$: it is not crystallizable. The salt commonly called *binarseniate of potassa* $=\text{KO},\text{AsO}_5$, may either be formed by adding excess of arsenic acid to solution of potassa, and evaporating; or by heating to redness, in a Florence flask, a mixture of equal parts of nitre and white arsenic; during the latter operation much nitrous gas is evolved, and on dissolving the residue in water, filtering, and evaporating, prismatic crystals are obtained, resembling those of the corresponding phosphates of ammonia and potassa: they are soluble in 5·3 parts of water at 40° , and insoluble in alcohol: their formula is $\text{KO},2\text{HO},\text{AsO}_5$. Macquer was the first who procured this salt: hence termed *Macquer's arsenical salt*. It is not easily decomposed by heat alone, and may be fused and kept red-hot without undergoing other change than losing a little acid; but when mixed with about an eighth of charcoal-powder and distilled, metallic arsenic rises, and carbonate of potassa, mixed with part of the charcoal, remains in the body of the retort. This salt, as well as the arsenite, is used for the cure of agues. It is a delicate test of the presence of silver, in solutions of which it occasions a red-brown precipitate: it is also sometimes used to separate iron from manganese; it produces in the persalts of iron a white precipitate, whilst the arseniate of manganese remains in solution.

ARSENIATES OF SODA. When an equivalent of arsenic acid is ignited with excess of carbonate of soda, 3 atoms of carbonic acid are expelled, and a tribasic arseniate of soda formed, which crystallizes from its solution with 24 atoms of water, forming the salt $3\text{NaO},\text{AsO}_3 + 24\text{HO}$, isomorphous with the corresponding phosphate of soda. The same salt is obtained by treating arsenic acid in solution with an excess of caustic soda. (GRAHAM.) When the bibasic arseniate is fused with excess of carbonate of soda, 1 atom of carbonic acid is expelled, and the tribasic salt formed. This salt forms rhombic prisms, alkaline, soluble in 3·57 of water at 60° , and losing, when heated in a platinum crucible, about 50 per cent. of water: the residue is fusible at a white-heat, and acts like soda upon glass.

When carbonate of soda is added to a hot solution of arsenic acid, so long as there is effervescence, a salt is obtained by evaporation correspond-

ing with the common phosphate of soda, and containing 2 atoms of soda and 1 of water, as bases: this salt affects the same two multiples, in its water of crystallization, as phosphate of soda, namely, 24HO , and 14HO ; but most frequently assumes the smaller proportion, forming the salt, $2\text{NaO}, \text{HO}, \text{AsO}_5 + 14\text{HO}$. This arseniate is more soluble than the phosphate, and slightly deliquescent in damp air. (GRAHAM.)

When to the last salt a quantity of arsenic acid is added, equal to what it already contains, and the solution is highly concentrated, the salt usually called *binarseniate of soda* crystallizes at a low temperature: this salt contains 1 atom of soda and 2 atoms of water as bases, with 2 atoms of water of crystallization, and corresponds with the so-called biphosphate of soda: its formula is $\text{NaO}, 2\text{HO}, \text{AsO}_5 + 2\text{HO}$. These arseniates of the alkalis, which contain water as base, all lose that element at a red-heat, but, unlike the phosphates, they recover it when again dissolved in water. Arsenic acid, therefore, forms only one, and that a tribasic class of salts. (GRAHAM.)

ARSENIATES OF LIME. When bibasic arseniate of soda is added to solution of chloride of calcium, the supernatant liquor becomes sour, and $3\text{CaO}, \text{AsO}_5$ is precipitated. (MITSCHERLICH.) The same salt falls on adding tribasic arseniate of soda to chloride of calcium. (GRAHAM.)

When arsenic acid, in slight excess, is added to lime water, a white powder falls, insoluble in water but soluble in dilute nitric and hydrochloric acids, and in acetate of ammonia, which is, after it has been exposed to a red-heat, $2\text{CaO}, \text{AsO}_5$. This compound, in a hydrated state, is found native, constituting the minerals called *Pharmacolite* and *Haidingerite*: the former is $2\text{CaO}, \text{HO}, \text{AsO}_5 + 5\text{HO}$ (according to Klaproth's analysis), and the latter $2\text{CaO}, \text{HO}, \text{AsO}_5 + 2\text{HO}$. (TURNER.)

The preceding arseniates of lime, when dissolved in excess of arsenic acid, afford small crystals on evaporating the solution, which are probably $\text{CaO}, 2\text{HO}, \text{AsO}_5$.

ARSENIATES OF BARYTA. When baryta water is added in excess to arsenic acid, or when tribasic phosphate of soda is dropped into excess of chloride of barium, and the precipitate quickly washed, a white powder falls which is almost insoluble in water, but readily soluble in hydrochloric and nitric acid: its formula, after exposure to heat, is $3\text{BaO}, \text{AsO}_5$. It contains about 68 *per cent.* of baryta and 32 of arsenic acid. (GRAHAM.)

When bibasic arseniate of soda is added to excess of chloride of barium, a crystalline deposit soon ensues, which when heated to redness is $2\text{BaO}, \text{AsO}_5$. Digested in water it is resolved into the preceding insoluble tribasic salt, and a monobasic arseniate remains in solution, which, after having been ignited, is BaO, AsO_5 .

ARSENIATES OF STRONTIA. When solutions of nitrate of strontia and bibasic arseniate of soda are mixed, a white insoluble powder falls: if the solutions be dilute a crystalline deposit is gradually formed $= 2\text{SrO}, \text{AsO}_5$. According to Thomson, the crystals include 8 atoms of water. This salt is readily soluble in aqueous arsenic acid.

ARSENIATES OF MAGNESIA. When sulphate of magnesia is precipi-

tated by bibasic arseniate of soda, a white powder falls, insoluble in water but soluble in nitric acid. When this salt is thrown down from a mixed solution of 3 parts of sulphate of magnesia and 5 of bibasic arseniate of soda, it contains 15 atoms of water, 12 of which are expelled at 212° , so that its formula is $2\text{MgO}, \text{HO}, \text{AsO}_5 + 2\text{HO} + 12\text{HO}$. (GRAHAM.) When solution of tribasic arseniate of ammonia is added to solution of sulphate of magnesia, a difficultly soluble crystalline precipitate falls which is an *ammonio-arsenate of magnesia* $= \text{NH}_4 \text{O}, 2\text{MgO}, \text{AsO}_5 + 12\text{HO}$. (WACH.)

ARSENIATES OF MANGANESE. When excess of protocarbonate of manganese is digested in solution of arsenic acid, a white crystalline powder is obtained $= 2\text{MnO}, \text{HO}, \text{AsO}_5$? The same salt may be formed by double decomposition. When a solution of protochloride of manganese with ammonia is added to a solution of arsenic acid, a flocculent precipitate of arseniate of manganese first falls, which afterwards passes into crystalline *ammonio-arsenate of manganese* $= \text{NH}_4 \text{O}, 2\text{MnO}, \text{AsO}_5 + 12\text{HO}$. (OTTO.)

ARSENIATES OF IRON. The protosalts of iron give a white precipitate with arseniate of ammonia, which gradually becomes green on exposure to air: it appears from Chenevix's analysis to be $3\text{FeO}, \text{AsO}_5 + 6\text{HO}$. When heated, it loses water, becomes first grey, then black, arsenious acid sublimes, and the residue is partly peroxide of iron. Protarsenate of iron is sparingly soluble in ammonia, and the solution acquires a green color by exposure. The *native cubic arseniate of iron* of Cornwall is $\text{FeO}, \text{Fe}_2 \text{O}_3, \text{AsO}_5 + 6\text{HO}$; and the *prismatic arseniate* or *Skorodite* of Brazil, is $2\text{FeO}, 2\text{Fe}_2 \text{O}_3, 3\text{AsO}_5, 12\text{HO}$. (BERZELIUS.) When solutions of perchloride of iron and bibasic arseniate of soda are mixed, a white *perarsenate of iron* falls: $2\text{Fe}_2 \text{Cl}_3 + 3[2\text{NaO}, \text{AsO}_5] = 2\text{Fe}_2 \text{O}_3, 3\text{AsO}_5 + 6\text{NaCl}$. This salt, when dried at common temperatures, retains about 18 *per cent.* of water ($= 12$ atoms) which it loses when heated, and becomes red, and at higher temperatures glows and acquires a yellow color. (Berzelius thinks that this indicates a change in the arsenic acid analogous to that of the phosphoric.) When freshly precipitated, it dissolves readily in ammonia forming a yellow or red solution, which, when evaporated, leaves a red basic double salt (*ammonio-arsenate*.) When protarsenate of iron is oxidized by digestion in nitric acid, and the solution evaporated to dryness or precipitated by ammonia, a *basic perarsenate* is obtained $= 2\text{Fe}_2 \text{O}_3, \text{AsO}_5$: this compound occurs *native* in combination with about 28 *per cent.* (12 atoms) of water. (BERZELIUS.) The stalactitic *pitch iron ore* is a hydrated persulphate and perarsenate of iron $= 4[\text{Fe}_2 \text{O}_3, \text{SO}_3] + 2\text{Fe}_2 \text{O}_3, 3\text{AsO}_5 + 45\text{HO}$. (STROMEYER.)

ARSENIATES OF ZINC. When bibasic arseniate of ammonia or soda is added to solution of sulphate of zinc, the liquor becomes sour and a tribasic arseniate of zinc falls in the form of a white powder soluble in arsenic and nitric acids. When zinc or oxide of zinc is dissolved in arsenic acid the solution yields cubic crystals on evaporation; or when fully saturated, a gelatinous residue. An *ammonio-arsenate of zinc* has been described by Bette. (*Ann. der Pharm.*, xv. 141.)

ARSENIATES OF TIN. The solution of tin in arsenic acid leaves a gelatinous residue on evaporation. A white powder is precipitated on adding arseniate of potassa to protochloride of tin.

ARSENIATE OF CADMIUM. Arseniate of potassa gives a white precipitate in dilute solutions of chloride of cadmium.

ARSENIATE OF COBALT falls as a pink precipitate on adding an alkaline arseniate to a soluble salt of cobalt: it occurs as a *native hydrate* in *peach blossom cobalt ore* $= 3\text{CoO}, \text{AsO}_5, 8\text{HO}$. (KERSTEN, *Poggend.*, LX.)

ARSENIATE OF NICKEL, formed by double decomposition, is a green powder, often granular and crystalline, insoluble in water, soluble in arsenic acid, and in ammonia. The mineral called *nickel ochre* is a *hydrated arseniate* $= 3\text{NiO}, \text{AsO}_5, 8\text{HO}$. (STROMEYER.)

ARSENIATES OF COPPER. When a bibasic alkaline arseniate is added to a salt of oxide of copper, a tribasic arseniate of copper $= 3\text{CuO}, \text{AsO}_5$ falls, the liquor becoming sour: it is a pale greenish-blue precipitate in its hydrated state: when heated it loses water, and becomes olive-green, without decomposition if kept out of contact of carbon: it is insoluble in the stronger acids and in ammonia. There are many *native subarseniates of copper* originally analysed by Chenevix. (*Phil. Trans.*, 1801.) The principal are *copper mica* $= 8\text{CuO}, \text{AsO}_5 + 12\text{HO}$; *Erinite*, analysed by Turner, $= 5\text{CuO}, \text{AsO}_5 + 2\text{HO}$; *radiated arseniate* $= 5\text{CuO}, \text{AsO}_5 + 5\text{HO}$; and *ferriferous arseniate* $= 2\text{CuO}, 3\text{FeO}, \text{AsO}_5 + 5\text{HO}$. *Kupferschaum* $= 5\text{CuO}, \text{AsO}_5 + 10\text{HO}$; *Olivenite* (arsenio-phosphate) $= 4\text{CuO}, [\text{AsO}_5, \text{PO}_5] + \text{HO}$; *Euchroite* $= 4\text{CuO}, \text{AsO}_5, + 7\text{HO}$; and *Lenticular ore*, which is an arsenio-phosphate, with aluminate of peroxide of iron, its formula, deduced from the analysis of Trolle Wachtmeister (*Poggend.*, xxv. 305) being $4\text{CuO}, [\text{AsO}_5, \text{PO}_5] + [\text{Al}_2 \text{O}_3, \text{Fe}_2 \text{O}_3] + 11\text{HO}$.

ARSENIATES OF LEAD. When acetate of lead is decomposed by bibasic arseniate of soda, a *tribasic arseniate of lead* falls, $= 3\text{PbO}, \text{AsO}_5$, and free acetic acid is found in the liquor: it is a white fusible salt, becoming yellow when heated, insoluble in water, but soluble in ammonia and ammoniacal salts. When arsenic acid, or a solution of a bibasic alkaline arseniate is dropped into solution of nitrate of lead, a white powder falls which is *bibasic arseniate of lead* $= 2\text{PbO}, \text{AsO}_5$: it is insoluble in water and in acetic acid, but soluble in nitric and in hydrochloric acid. It occurs *native*.

ARSENIATE OF ANTIMONY. Arseniate of potassa throws down a white precipitate in the hydrochloric solution of oxide of antimony.

ARSENIATE OF BISMUTH falls in the form of a white powder on adding arsenic acid to the nitric solution of bismuth: it is insoluble in water, but soluble in hydrochloric acid.

ARSENIATE OF URANIUM is thrown down, of a straw color, when per-nitrate of uranium is decomposed by arseniate of potassa.

ARSENIC AND CHLORINE. CHLORIDE OF ARSENIC. AsCl_3 . This compound may be formed : 1. By throwing finely-powdered arsenic into chlorine; the metal burns and produces a volatile liquid : or by passing dry chlorine over arsenic placed in a curved tube or adopter, and gently heated: the resulting vapor of the chloride should be condensed in a receiver cooled by ice, and may be purified by redistilling it off a little powdered arsenic. 2. Distil 6 parts of corrosive sublimate with 1 of powdered arsenic; the chloride passes into the receiver in the form of an unctuous fluid, formerly called *butter of arsenic*. 3. 1 part of arsenious acid with 10 parts of sulphuric acid, are put into a tubulated retort, and the temperature raised to about 212° . Fragments of fused common salt are then thrown in by the tubulature; by continuing the heat, and successively adding the salt, chloride of arsenic is obtained; it distils over, and may be condensed in cold vessels. Very little hydrochloric acid is disengaged, but towards the end of the operation, a portion of hydrated chloride of arsenic is produced, which floats upon the pure chloride, and appears more viscid and colorless; it may be deprived of water by redistillation with concentrated sulphuric acid. Mixed with a larger quantity of water, the chloride of arsenic is decomposed, and arsenious acid is formed, hydrochloric acid being at the same time produced.

Chloride of arsenic is a dense oleaginous transparent liquid: it does not freeze at 0° ; it boils at about 270° , the density of its vapor being 6.3: it exhales vapor when exposed at common temperatures to the air; with a small quantity of water it forms what has been termed *hydrated chloride of arsenic*; this is probably a hydrochloric solution of arsenious acid; $[\text{AsCl}_3 + 3\text{HO} = \text{AsO}_3 + 3\text{HCl}]$, and when more largely diluted, arsenious acid is deposited; but when a solution of arsenious acid in excess of hydrochloric acid is heated, the whole volatilizes and there is no residue, so that when hydrochloric acid containing arsenious acid is distilled, the product which passes over is arseniferous; and when arseniferous acid acts upon common salt, the hydrochloric acid which is evolved carries the arsenic with it.

When sulphur or phosphorus are heated in this chloride they are dissolved, but again deposited on cooling. It is decomposed by iron, zinc, cadmium, tin, lead, copper, antimony, and bismuth. It combines with oil of turpentine and with olive-oil. It absorbs about ten times its volume of chlorocarbonic acid, but gives it off again on dilution with water. Chloride of arsenic consists of

						J. Davy.
Arsenic	1	75	40.98 39.52
Chlorine	3	108	59.02 60.48
<hr/>			<hr/>	<hr/>	<hr/>	
Chloride of arsenic.....	1		183		100.00	100.00
<hr/>						
		Vols.		Sp. gr.	Vols.	Sp. gr.
Arsenic vapor	1	10.39	} = {	$\frac{1}{4}$ 2.59
Chlorine gas	6	14.73		$1\frac{1}{2}$ 3.68
<hr/>			<hr/>	<hr/>	<hr/>	
Vapor of chloride of arsenic	4		25.12		1	6.27

No chloride corresponding with arsenic acid has been obtained; when excess of chlorine is passed over arsenic, a white crystalline sublimate sometimes makes its appearance, which was regarded as a perchloride,

but which is arsenious acid dependent for its formation upon moisture in the chlorine. When a mixture of arsenic and calomel is distilled, a dark-brown sublimate is obtained, which is said to be a mixture of calomel with a *subchloride* of arsenic.

IODIDE OF ARSENIC. AsI_3 , obtained by heating 1 part of arsenic with 3 or 4 of iodine, is of a deep red color, and volatile, so that it may be purified by sublimation. When acted upon by water, it produces hydriodic and arsenious acids; and on evaporating the solution a compound of arsenious acid and iodide of arsenic is obtained in nacreous crystals. (PLISSON. SERULLAS. HOTTOT. *Journ. de Pharm.*, Jan. and March, 1828.) According to Bette a pure iodide of arsenic is obtained by fusing together about 3 parts of finely-powdered arsenic and 10 of iodine, digesting the mass in hot alcohol, filtering and setting aside to crystallize: it forms red lamellar crystals, which fuse and sublime when heated. It consists of

						Plisson.	Bette.
Arsenic	1	75	16.56	16.4
Iodine	3	378	83.44	83.6
<hr/>			<hr/>		<hr/>		<hr/>
Iodide of arsenic	1		453		100.00		100.00

BROMIDE OF ARSENIC. AsBr_3 . Bromine and arsenic act intensely on each other with the evolution of heat and light, and form a crystallizable compound which fuses at 70° , and boils and evaporates at 430° . By the action of water, it yields arsenious and hydrobromic acids, and on evaporation, crystals of a pearly lustre are formed, which consist of arsenious acid in combination with the bromide. (SERULLAS, *Ann. Ch. et Ph.*, xxxviii. 318.)

FLUORIDE OF ARSENIC. AsF_3 , is obtained by distilling a mixture of 5 parts of powdered fluor spar with 4 of arsenious acid and 8 of sulphuric acid. A colorless fuming liquid passes over, which is decomposed by water, and by the contact of glass. Unverdorben, who first examined this compound, states its specific gravity to be 2.73. It is extremely volatile, and fumes in the air. The specific gravity of its vapor exceeds 4. It combines without decomposition with ammonia. In the above process, silicated fluoric acid is also formed at the expense of the glass retort, but escapes in the gaseous form, while the fluoride of arsenic may be condensed in a bent tube surrounded by ice. (*Poggend.*, vii. 316.)

ARSENIC AND HYDROGEN. When arsenic is made the negative pole in water, of a powerful voltaic battery, a brown substance is deposited, which evolves hydrogen when heated, and easily burns in the air. The same substance is formed during the action of an alloy of arsenic and potassium or sodium upon water. (DAVY.) It appears from Soubeiran's experiments to be $= \text{AsH}_2$.

ARSENURETED HYDROGEN GAS. AsH_3 . When nascent hydrogen comes into contact with arsenic or with any of its compounds, a portion of the metal is carried over in the gaseous form, giving the hydrogen an alliaceous odor, causing it to burn with a peculiar blue-tinted flame, and to

give off arsenious acid during its perfect combustion, or to deposit upon cold substances held in its flame a film of metallic arsenic. These and other indications of the presence of arsenic are evident when only a very minute portion of the metal is present, hence their value in detecting it in the processes which will presently be described.

When arsenious acid is added to dilute sulphuric acid, and zinc dissolved in the mixture, the liberated hydrogen is rich in arsenic; but in this case a considerable proportion of free hydrogen also is evolved. Pure arsenuretted hydrogen is best obtained by the action of hydrochloric acid upon a pulverized alloy of zinc and arsenic, obtained by fusing together equal parts of those metals in an earthen retort or covered crucible. The gas is colorless: it has a nauseous odor, and is alarmingly poisonous, so that even when largely mixed with air it excites nausea, vomiting, giddiness, and other dangerous symptoms; too much caution cannot therefore be observed in dealing with it. It has proved fatal to two chemists, namely, Gehlen and Bullacke: Gehlen, suspecting that the gas was escaping from some part of the apparatus he was using, applied his nose for the purpose of detecting it, and although he inhaled a very small quantity, he was seized in about an hour with shivering fits and vomiting, attended by extreme debility, and although every medical aid was resorted to, died on the ninth day. (*Ann. Ch. et Ph.*, iii. 135.) Bullacke lingered under similar symptoms for twelve days.

The specific gravity of arsenuretted hydrogen is 2.695: it may be collected and retained over water, which however absorbs it to the amount of about one-fifth its volume, and if it contain air, a thin film of metallic arsenic is gradually deposited: it is not absorbed by alkaline solutions nor by alcohol or ether, but oil of turpentine absorbs it largely, and the fat oils sparingly. It is liquified, under atmospheric pressure, when cooled down to -40° . (DUMAS and SOUBEIRAN, *Ann. Ch. et Ph.*, xliii.) Faraday could not solidify it at 166° below 0° . He found the tension of its vapor at $-70^{\circ}=1.08$ atmospheres, at $-60^{\circ}=1.40$, at $-50^{\circ}=1.80$, at $-40^{\circ}=2.28$, at $-30^{\circ}=3.24$ at $-20^{\circ}=3.51$, at $-10^{\circ}=4.30$, at $0^{\circ}=5.21$, at $32^{\circ}=8.95$, and at $60^{\circ}=13.19$ atmospheres. (*Ph. Tr.*, 1845, p. 170.)

Arsenuretted hydrogen is decomposed at a red-heat, arsenic is deposited, and 1 volume of the gas affords 1.5 of hydrogen. When mixed with an insufficient quantity of air or of oxygen for its perfect combustion, it deposits metallic arsenic when burned; but with excess of oxygen it explodes with violence and forms water and arsenious acid: it burns in contact of air with a pale blue flame, forming water and arsenious acid, and depositing arsenic upon the sides of the jar as the flame descends. For its perfect combustion it requires 1.5 volume of oxygen; or 4 volumes require 6 of oxygen: its components being

					Vols.	Sp. gr.	Vols.	Sp. gr.
Arsenic	1	75	96.15	Arsenic vapor....	1	10.399	= 0.25	2.599
Hydrogen.....	3	3	3.85	Hydrogen gas	6	0.416	= 1.50	0.104
<hr/>								
Arsenuretted } hydrogen.... }	1	78	100.00	Arsenuretted } hydrogen gas }	4	10.815	= 1.	2.703

Arsenuretted hydrogen gas is instantly decomposed by chlorine; and if chlorine be suffered to ascend into a jar containing it, and standing

over water, each bubble inflames, producing hydrochloric acid, and brown fumes of arsenic are deposited ; if the arsenuretted hydrogen be sent up in the same way into chlorine, there being great excess of the latter, hydrochloric and arsenious acids are immediately formed. The gas is similarly but less intensely decomposed by iodine and bromine. Fuming nitric acid immediately and violently acts upon and oxidizes it, and sometimes with inflammation. When sulphur and phosphorus are heated in it, sulphuretted and phosphuretted hydrogen and sulphuret and phosphuret of arsenic are formed, and it is also decomposed when heated in contact with potassium and sodium, and with tin and zinc. With solution of corrosive sublimate arsenuretted hydrogen gives a precipitate composed, according to Rose, of 1 atom of arsenic, 6 of mercury, and 3 of chlorine. Agitated with solution of sulphate of copper the gas is absorbed, and arsenuret of copper and water are formed. $3[\text{CuO}, \text{SO}_3] + \text{AsH}_3 = \text{Cu}_3\text{As} + 3\text{HO} + 3\text{SO}_3$. This action furnishes a good means of testing the purity of the gas, for any uncombined hydrogen remains unacted on. It reduces the salts of silver, gold, platinum, and rhodium, and arsenious acid remains in solution : thus, with nitrate of silver, the results are silver, arsenious acid, water, and nitric acid. $6[\text{AgO}, \text{NO}_5] + \text{AsH}_3 = 6\text{Ag} + \text{AsO}_3 + 3\text{HO} + 6\text{NO}_5$. Arsenuretted hydrogen does not decompose the salts of iron, nor does it produce any change in solution of emetic tartar, or of acetate of lead.

ARSENIC AND SULPHUR. PROTOSULPHURET OF ARSENIC. RED SULPHURET OF ARSENIC. REALGAR. AsS_2 . By slowly fusing a mixture of metallic arsenic and sulphur, or of orpiment and arsenious acid, or by heating arsenious acid, charcoal, and sulphur, a *red sulphuret of arsenic* is obtained. It is crystallizable, and of a vitreous fracture: its specific gravity is 3·4 to 3·5. It is easily fusible, and may be sublimed, unaltered, in close vessels.

It is usually known under the name of *Realgar*, and occurs *native* in Germany and Switzerland, in veins of primitive rocks and among volcanic products. Its primary form is an acute octohedron. It is used in the preparation of the pyrotechnical compound, called *White Indian Fire*, which consists of 24 parts of saltpetre, 7 of sulphur, and 2 of realgar, finely powdered and well mixed: it burns with a white flame of great brilliancy. When this sulphuret is digested in a solution of caustic potassa, a part of its sulphur is removed, and a black or brown powder remains, which, when heated, is resolved into realgar and metallic arsenic, and which is regarded as a *subsulphuret*. Realgar consists of

						Native.	
						Klaproth.	Laugier.
Arsenic	1	75	70·09 69 69·57
Sulphur	2	32	29·91 31 30·43
<hr/>						<hr/>	<hr/>
Realgar	1		107		100·00	100	100·00

SESQUISULPHURET OF ARSENIC. YELLOW SULPHURET OF ARSENIC. ORPIMENT. SULPHARSENIOUS ACID. AsS_3 . When realgar is fused with sulphur, or when sulphuretted hydrogen is passed through a solution of arsenious acid in dilute hydrochloric acid, this sulphuret is formed: in the latter case it is in the form of a yellow powder. It is fusible, and

assumes a lamellar or crystalline texture on cooling, and may be sublimed without decomposition in close vessels. Heated in the air, it burns with a pale-blue flame, exhaling white fumes and the odor of sulphurous acid. Its specific gravity is 3.45. It sparingly dissolves in boiling water. It is soluble in caustic alkaline solutions; it is insoluble in acids, but is decomposed by nitric and nitrohydrochloric acids. These sulphurets are readily decomposed by fusion with potassa; sulphuret of potassium and a sublimate of metallic arsenic are the results.

Braconnot has employed an *ammoniacal solution of orpiment* as a dye-stuff (*Ann. de Ch. et Ph.*, xii.); the process he recommends is as follows: 1 part of sulphur, 2 of white arsenic, and 5 of pearlash, are to be fused in a crucible at a heat a little below redness: a yellow mass results which is to be dissolved in hot water and filtered; the filtered solution, diluted with water, is to be treated with weak sulphuric acid, and will give a fine yellow precipitate, which easily dissolves in ammonia, forming a solution at first yellow, but becoming colorless on adding more ammonia. The wool, silk, cotton, or linen, is to be dipped into this solution, more or less diluted according to the color required, care being taken that no metallic vessels are used; on taking them out they are at first colorless, but, as the ammonia evaporates, become yellow; they are then to be freely exposed to the air, washed, and dried. This color is very permanent, but soap impairs it. Orpiment is also the basis of the pigment called *King's Yellow*. The composition of orpiment is

						<i>Native.</i>			
						Berzelius.	Laugier.	Klaproth.	
Arsenic	1	...	75	...	60·98	...	61·86	...	62
Sulphur	3	...	48	...	39·02	...	38·14	...	38
<hr/>						<hr/>			
Orpiment	1		123		100·00	100	100·00		100

Native Orpiment (the *auripigmentum* of the ancients) is of a bright lemon or golden color. It is generally massive and lamellar. It occurs both in primitive and secondary rocks in Suabia, Hungary, China, and South America.

PERSULPHURET OF ARSENIC. SULPHARSENIC ACID. AsS_5 . When sulphuretted hydrogen is passed through a concentrated solution of arsenic acid, a yellow precipitate slowly falls, which resembles orpiment in color, and, like it, may be sublimed without change, in close vessels; it also is easily fusible, and soluble in alkaline solutions, but insoluble in boiling water. The same compound is obtained when sulphuretted hydrogen is passed through a concentrated solution of arseniate of potassa, and the resulting sulpho-salt decomposed by hydrochloric acid. This sulphuret of arsenic consists of

						Berzelius.
Arsenic	1	...	75	...	48.39 48.3
Sulphur	5	...	80	...	51.61 51.7
<hr/>						<hr/>
Persulphuret of arsenic	1		155		100.00	100.0

According to Berzelius, there is a compound of arsenic with a larger relative quantity of sulphur, which is formed when a neutral solution of arsenio-persulphuret of potassium is mixed with alcohol, and filtered; the filtered solution is reduced by distillation to somewhat less than half its

bulk, and suffered to cool slowly, when it deposits crystalline scales, which are as fusible as sulphur itself, and which he regards as a definite compound of arsenic, with great excess of sulphur. (*Lehrbuch*, ii. 44.)

The sulphurets of arsenic are all poisonous, though less virulent than the oxides. (ORFILA.) They combine with sulphur, or are soluble in fused sulphur, in all proportions.

ARSENIO-SULPHURETS. Each of the preceding sulphurets of arsenic combines, as a *sulphur-acid*, with the opposed, or electropositive sulphurets, or sulphur-bases, to form a class of *sulphur-salts*, called, by Berzelius, *Arsenio-sulphurets*: hence we have three classes of these salts, namely, the *arsenio-protosulphurets*, the *arsenio-tersulphurets*, and the *arsenio-persulphurets*.

1. The *arsenio-protosulphurets* (containing realgar, or protosulphuret of arsenic,) are formed, in the dry way, when sulphur-bases are fused with realgar; or when the arsenio-tersulphurets are fused with metallic arsenic: when thus obtained, they are decomposed by water, which causes the separation of a black or brown subsulphuret of arsenic, and the residue is an arsenio-tersulphuret. These salts cannot be obtained by the direct action of caustic alkali, or of hydrosulphuret, upon realgar; for in that case, also, an arsenio-tersulphuret and black subsulphuret are formed: but they are produced by boiling orpiment in a somewhat concentrated solution of carbonate of potassa, or of soda, and filtering the solution whilst hot; it becomes turbid as it cools, and a brown flocculent precipitate falls, which is a neutral compound of the alkaline sulphuret with realgar, that is, an *arsenio-protosulphuret of potassium*, or of *sodium*. These salts are red or brown, and mostly insoluble in water. The acids decompose them, and separate realgar.

2. The *arsenio-tersulphurets* (containing orpiment, or tersulphuret of arsenic,) can only be obtained in the dry way, and in a solid state, for when their solutions are evaporated to a certain degree of concentration, a brown powder is deposited (which is an arsenio-protosulphuret,) and an arsenio-tersulphuret, with excess of base, remains in solution: but the decomposition is not perfect, till the latter salt crystallizes. By dilution with water, and boiling, the precipitate is redissolved, and the arsenio-tersulphuret reproduced. When orpiment is digested in weak caustic alkali at common temperatures, a compound, containing twice the quantity of orpiment that exists in the neutral compound, is obtained. The arsenio-tersulphurets of the alkaline bases are not decomposed by dry distillation; the others are decomposed at a red-heat, orpiment is given off, and the sulphur-base remains.

3. *Arsenio-persulphurets*, (containing the persulphuret of arsenic.) These compounds vary in color; their taste is hepatic, and extremely nauseous and bitter; decomposed by an acid, they give out a very peculiar hepatic odor: when the base is a sulphuret of the metals of the alkalis or alkaline earths, or of glucium or yttrium, or of a few of the other metals, these salts are soluble in water; the others are insoluble. These salts are often *basic*, and are then mostly crystallizable, which is rarely the case with the *neutral* compounds; the latter are decomposed by dry distillation, and resolved into arsenio-sesquisulphurets and sulphur; but the basic compounds remain unchanged. They are easily

decomposed in the open fire. The concentrated solutions of these salts are only very slowly decomposed by exposure to air; when more dilute, they gradually become turbid, and deposit sulphur and sulphuret of arsenic, whilst the solution contains undecomposed salt, together with arsenites and hyposulphites, which, after complete decomposition, become sulphates*.

SULPHURET OF ARSENIC AND IRON, FeAs,FeS_2 , is found native in many parts of Europe. It is of a more silvery color than iron pyrites, and when heated exhales arsenic. It is called *arsenical pyrites* or *mis-pickel*, and is an abundant source of arsenious acid. It appears to be a compound of a bisulphuret of iron with arsenuret of iron; or,

					Chevreul.	Stromeyer.
Iron	2	56	34.35	34.938	36.04	
Arsenic	1	75	46.01	43.418	42.88	
Sulphur.....	2	32	19.64	20.132	21.08	
<hr/>						
Sulphuret of arsenic and iron	1	163	100.00	98.488	100.00	

PHOSPHURET OF ARSENIC is obtained by heating equal parts of arsenic and phosphorus: it forms a dark-brown metallic sublimate. (LANDGREBE.)

SELENIURET OF ARSENIC is formed by dissolving arsenic in fused selenium: it is a black fusible compound, less volatile than its components, so that excess of either may be driven off by heat. At a red-heat it boils and sublimes. (BERZELIUS.)

ALLOYS OF ARSENIC. ARSENURETS. Arsenic unites with most of the metals, forming compounds which are generally brittle and comparatively fusible. With *potassium* it forms by fusion a brownish compound, which, when put into water, evolves less hydrogen than pure potassium, in consequence of the formation of hydruet of arsenic. When potassium is heated in arsenuretted hydrogen, hydrogen is evolved, and arsenuret of potassium formed. (DAVY.) With *sodium*, the alloy is either brown and of an earthy aspect, or grey and metallic, according to the proportions of the metals: water acts upon it as upon the former. (GAY LUSSAC and THENARD, *Recherches Physico-Chimiques*, i.) The alloy of arsenic and *manganese* exists *native*: it resembles pyrolusite; its sp. gr. 5.5; hard and grey, becoming black by exposure; it dissolves in nitrohydrochloric acid, and appears, from Kane's analysis, to be Mn_2As . (*Quart. Journ.*, N.S., vi. 381.) Arsenic and *iron* form compounds which are more brittle, hard, and fusible than iron: when iron only contains

* Having stated thus much respecting the arsenio-sulphurets, I shall not go into the details of their history, or attempt a description of their manifold varieties; of these the reader may form some notion, by reference to Dr. Turner's abstract of the properties of a few of the leading *arsenio-persulphurets* only, (*Elem. of Chem.*, p. 753,) or he may consult Berzelius or Gmelin

for a full account of them. The question as to the state of these compounds when in aqueous solution, is involved in the same difficulties with that respecting the solutions of the sulphurets of the alkaline bases, and admits of similar explanation. See also in reference to a new class of these salts, a paper by Bouquet and Cloez. (*Ann. Ch. et Ph.*, January, 1845.)

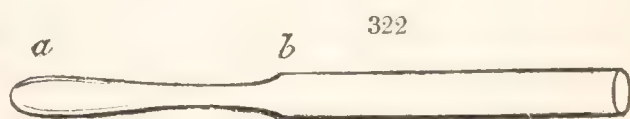
2 or 3 *per cent.* of arsenic, it becomes very brittle when heated. With the acids these arsenurets evolve arsenuretted hydrogen; they retain their influence upon the magnet till the arsenic forms about 50 *per cent.* The compound FeAs is found *native* in rhombic prisms; sp. gr. 7.22: it is of a grey color, and gives a black powder. Arsenuret of *zinc* is obtained by placing some arsenic at the bottom of a crucible, or coated retort, and covering it with its weight of granulated zinc; the temperature is gradually raised till the alloy is fused; it is grey, brittle, and granular in texture; with hydrochloric acid it yields chloride of zinc and arsenuretted hydrogen; it contains 43.7 arsenic and 56.3 zinc. (SOUBEIRAN.) Arsenuret of *tin* is formed by fusion; it is brilliant, crystalline, and brittle. According to Dumas, the most perfectly crystalline compound is 86 *per cent.* of tin and 14 arsenic. Arsenuret of *cobalt* is formed by heating arseniate of cobalt with charcoal, or in hydrogen gas; or arsenic and cobalt may be fused together; the resulting compound contains 38.5 arsenic + 61.5 cobalt. The *native arsenuret of cobalt* has already been mentioned as one of the ores of that metal: it occurs in cubic, octohedral, and dodecahedral crystals, sp. gr. 6.78, of a tin white color; it contains about 20 *per cent.* of cobalt and 80 arsenic, and is therefore Co_2As_3 . The ore known in Germany as *speiskobalt*, is an arsenuret of cobalt, iron, and nickel. Arsenuret of *nickel* is made by heating to bright redness arseniate of nickel in a crucible lined with charcoal: a fused button is obtained which is grey and brittle. (BERTHIER.) *Kupfernickel* is a *native arsenuret* $= \text{AsNi}_2$; one of the crystallized arsenurets appears to be AsNi_3 ; and the white arsenical nickel, or *nickel pyrites*, is AsNi . When *copper* is heated to redness with excess of arsenic, a grey arsenuret is formed: it is granular and brittle; it has been called *white tombac*. When arsenuretted hydrogen is passed through a solution of copper, a black arsenuret is formed $= \text{Cu}_3\text{As}$: when passed over dry chloride of copper, hydrochloric acid is evolved, and the same compound formed. $3\text{CuCl} + \text{AsH}_3 = \text{Cu}_3\text{As} + 3\text{HCl}$. (KANE.) Arsenuret of *lead* is obtained by heating lead with excess of arsenic or of arsenious acid: in the latter case arseniate and arsenuret of lead are the results; it is a grey, crystalline, brittle compound, not entirely decomposed by heat; it contains about a sixth of its weight of arsenic. A very minute quantity of arsenic (less than 1 *per cent.*) is always contained in common lead shot; it gives the lead the property of spherical granulation, when the fused metal is passed through a sieve and suffered to fall through the air till it solidifies. Arsenuret of *antimony* is brittle, hard, and very fusible: it occurs *native*, containing, according to Rammelsberg, about 36 *per cent.* of antimony; this ore therefore is SbAs_3 . Arsenuret of *bismuth* has not been satisfactorily examined, nor are the alloys of arsenic with uranium, titanium, cerium, or tellurium, known.

TESTS FOR ARSENIC. As arsenic, either accidentally or intentionally taken, is a frequent cause of death, and often the subject of judicial inquiry, it becomes of importance to point out the most effectual modes of discovering its presence. Where arsenic proves fatal it is not always found in the contents of the stomach after death, but is often previously voided by vomiting or by stool; and it may sometimes be detected in the matters thrown off the stomach, in the form of a white powder, subsiding

in water. The inflammation of the stomach which results is generally a secondary effect, and takes place whether the poison be swallowed or applied to a wound. If minute quantities of white powder be detected in the stomach after death, or in the matter vomited, it may be treated as follows:

(a.) Mix a small portion of it with about two parts of black flux; introduce the mixture into a glass tube, and gradually heat it red-hot in the flame of a spirit-lamp. If arsenic be present, a *steel-colored sublimate* will attach itself to the cooler part of the tube, which, when heated, evaporates in fumes *strongly smelling of garlic*. If the metallic arsenic be heated in a tube open at both ends, and held so that a current of air may traverse it, it becomes converted into *arsenious acid*, which deposits itself in minute but characteristic *octohedral crystals*, easily recognized by the aid of a lens, or microscope.

Berzelius recommends the atom of white arsenic (or other arsenical compound) to be introduced into the bottom *a* of a tube, shaped as in the margin, and covered up to *b* with powdered charcoal, previously heated before the blow-pipe, to expel all moisture. Heat is then so applied by the flame of a spirit-lamp as to make the charcoal red-hot; the portion *a* is then heated, and the vapor of the white arsenic is decomposed as it passes through the red-hot charcoal, and a metallic film of arsenic deposited in the cold part of the tube. The bottom of the tube is then cut off, and the arsenic recognised as before, by the alliaceous smell of its vapor, and by its reconversion into arsenious acid.



(b.) Boil the suspected matter in a little distilled water, and when the liquor has cooled, slightly acidulate it by a drop or two of hydrochloric acid; then add a strong solution of sulphuretted hydrogen, or pass the gas through it. If arsenic be present, a *yellow precipitate* will appear. The hydrosulphuretted alkalis do not affect the arsenious solution unless a drop or two of acetic or hydrochloric acid be added, when the yellow precipitate falls; these tests are, however, equivocal, where very small quantities are to be detected, for if slight excess of alkali be present, it retains the sulphuret in solution, and excess of acid sometimes occasions a little sulphur to fall.

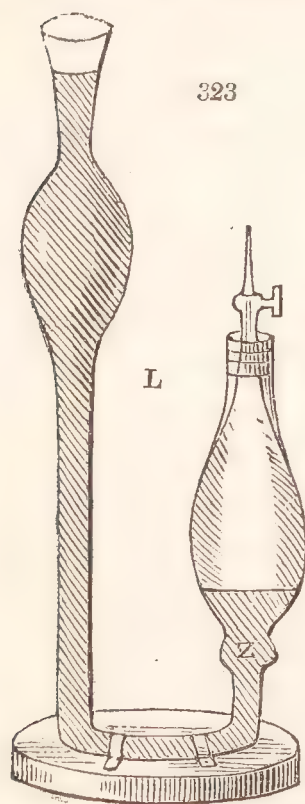
(c.) To the solution *b* add a drop of solution of carbonate of potassa, and then a drop or two of solution of sulphate of copper. An *apple-green precipitate*, commonly known as *Scheele's Green*, indicates arsenic. The ammonio-sulphate and ammonio-acetate of copper also give the peculiar green precipitate when added to very dilute solutions of white arsenic. This test, however, is fallacious when applied to mixed fluids, for the ammoniacal solution of sulphate of copper produces in some vegetable and animal infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas, in other mixed fluids, such as tea and porter, to which minute quantities of arsenic have been added, it occasions none at all. In some of those liquids a free vegetable acid may be the solvent, but the arsenite of copper is also dissolved by tannin, and perhaps by other vegetable, as well as some animal principles. (TURNER.)

(d.) Add to the solution *b* a drop of nitrate of silver and of solution

of ammonia, or of ammonio-nitrate of silver; a *yellow precipitate* indicates arsenic. This precipitate must be distinguished from that arising from phosphoric acid or phosphates.

(e.) The Voltaic pile, made to act by two wires on a little arsenious solution placed upon a piece of glass, develops metallic arsenic at the negative pole; and if this wire be of copper it becomes whitened by metallic arsenic, which may be further identified as mentioned under Reinsch's test.

(f.) Marsh has ingeniously availed himself of the affinity of hydrogen for the detection of arsenic. It has been above remarked that when hydrogen is generated in contact of any arsenical combination, it combines with the metal to form arsenuretted hydrogen gas, and the presence of a very minute trace of arsenic in hydrogen may be detected by burning it so that the flame may come into the *contact* of a plate of glass, or what answers better, of a piece of white earthenware, such as a common plate; it then deposits a dark metallic spot; or if a cold substance be held a little *above* the flame, arsenious acid condenses upon it; in these cases, the garlic odor of arsenic is perceptible, and if paper has upon it the slightest deposit of white arsenic, it gives a yellow tint when touched with a little diluted ammonio-nitrate of silver. Arsenuretted hydrogen may also be recognized by its blackening effect upon solutions of copper and silver, but sulphuretted hydrogen occasions a similar change. The ap-



paratus for this detection of arsenic is represented in the margin. When it is used, the stopcock, which is fitted into the lower bulb by grinding, is removed, and a piece of *pure* zinc placed at *z*; the bulb and tube are then filled to the level *L* with the liquid to be tested, to which a sufficiency of pure dilute sulphuric acid is previously added, the stopcock is replaced, hydrogen gas is soon liberated, and filling the lower bulb presses the liquid into the upper one; the gas being now under pressure, may be allowed to issue in a very small jet from the stopcock, and being inflamed may be tested by holding a piece of white earthenware *in* the flame, and a piece of writing paper an inch or two above it, when the indications of arsenic above mentioned will be observed, provided that metal exists in the tested liquid. The zinc and the acid used in these experiments should be previously examined as to their purity, for either may contain traces of arsenic; the zinc may also contain antimony,

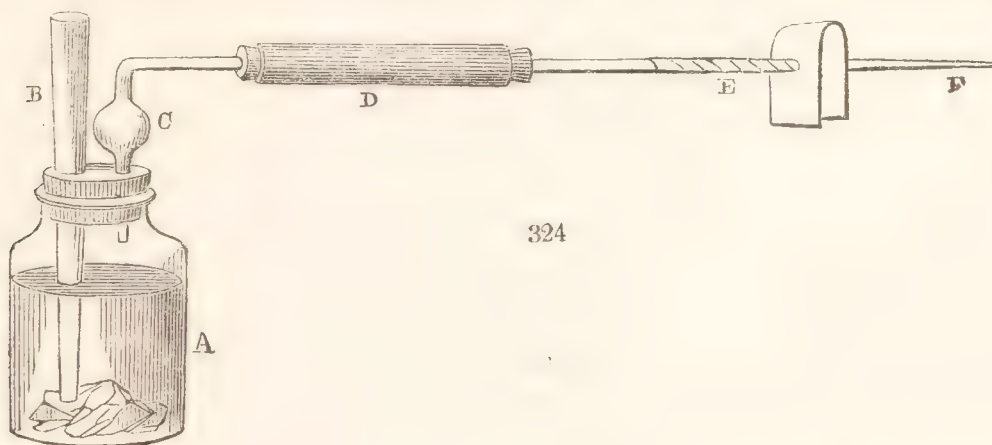
or antimony may by possibility be present in the tested liquid, in which case, appearances resembling those of arsenic will ensue, for antimony also goes off with the hydrogen; but there is then neither the garlic odor, nor any indications of arsenic by the silver test: if the flame from the jet be received into a piece of glass tube the depositions may be more precisely examined, and the metallic film of arsenic may be so heated as to be converted in arsenious acid. In regard to the differences between the stain from arsenic and that from antimony, it may be observed that the former when received on glass is *nut-brown* by transmitted light, while that from antimony is *grey-black*; both are opaque

in the centre. (See also in reference to the distinction between antimony and arsenic, a method proposed by Fresenius, *Ann. der Chem. und Pharm.*, Sept. 1842; and *Chem. Gaz.*, Jan. 1843; and a paper by Meissner, *ibid.*, July, 1843.) If the substances under examination are blended with organic matters, these should be got rid of as far as possible by filtration, or by the other usual methods employed in such cases.

There is a useful memoir on the tests for arsenic in the *Ann. Ch. et Ph.*, for June, 1841 (II., 159, 3me Serie), being a report by Thenard, Dumas, Boussingault, and Regnault; from which it appears that when properly applied, Marsh's test is so sensible as to indicate the presence of from 1 to a 2-millionth part of arsenic contained in solution; before the gas is burned so as to produce the arsenical deposit, they recommend passing it through a short glass tube containing amianthus or cotton, to prevent the possibility of minute portions of the liquid being carried up mechanically, and which may leave small spots of oxysulphuret of zinc liable to be mistaken for arsenic.

The following is the form of apparatus which they prefer:

A is the generating bottle about four-fifths filled with the liquid to be tested; it should contain some pieces of pure zinc, and the requisite sulphuric acid may be added by the tube B; the gas escapes through C, and passes through the amianthus in D, into the smaller tube, E, part of which is protected by copper-foil, and the end, F, drawn out into a capillary opening. The gas, as it passes through E, is decomposed by heating



the protected part of the tube to redness, the extension of the heat to F being prevented by the piece of bent metal plate on E. The film of arsenic deposited in the cool part of the tube may be examined as to its volatility and its conversion into arsenious acid, when heated in the tube open at both ends, &c. The gas may also be burned in the usual way at the capillary end, F. (On the *quantitative* determination of arsenic, see FRESSENIUS, *Mem. Ch. Soc.*, II. 129.)

(g.) *Reinsch's test* is an extremely delicate and simple means of detecting the presence of arsenic, and is especially valuable when the presence of organic matter interferes, either as affecting the color of the precipitates with copper, silver, and sulphuretted hydrogen, or by occasioning viscosity and froth where Marsh's test is used: it consists in adding a few drops of muriatic acid to the suspected solution and then placing in it a slip of bright copper, and heating up to the boiling-point, when if arsenic be present the copper acquires a grey color from the deposit of that metal: remove the slip of copper, wash and dry it carefully, and heat it in a glass tube, when a sublimate of arsenious acid will be obtained.

“This test failed to detect the four-thousandth part of a grain of arsenic in thirty drops of water, the dilution being equal to 120,000 times the weight of the arsenic. The deposit on copper commenced with a violet-colored film when the quantity of arsenious acid was equal to the 3000th part of a grain in 30 drops of water, or under a dilution of 90,000 times its weight: it was also very decided with the 2000th part of a grain in the same quantity of water; but in neither of these cases could octohedral crystals of arsenious acid be obtained by heating the copper.” (TAYLOR.) Several other metals produce an appearance more or less resembling that of arsenic when thus tested by copper, so that in this, as in all other cases, the formation of arsenious acid and its subsequent reduction, and the collateral evidence of the other tests, must be resorted to; but it is an excellent and easy method of separating the arsenic.

For further details upon this subject, especially in reference to the various modes which have been suggested of getting rid of organic matter, to the relative delicacy and fallacies of the various tests, and to the quibbles which are apt to arise in courts of law, I must refer to writers on toxicology and medical jurisprudence. (PARIS and FONBLANC. CHRISTISON. A. TAYLOR, GUY, &c.)

§ XXV. MOLYBDENUM. Mo. 48.

THE sulphuret is the most common natural compound of this metal: from this ore the *molybdic acid* was first obtained by Scheele in 1778 (*Opuscula* I.) and from this the metal was obtained by Hielm in 1782. (*Crell's Ann.*) To procure the metal, the native sulphuret is powdered and exposed under a muffle, moderately heated, till converted into a grey powder, which is to be digested in ammonia, and the solution filtered and evaporated to dryness. The residuum is dissolved in nitric acid, re-evaporated to dryness, and violently heated with charcoal. Metallic molybdenum is best obtained by passing a current of dry hydrogen gas over molybdic acid heated to whiteness in a porcelain tube. It should be suffered to cool in the contact of hydrogen. (BERZELIUS.)

The metal is of a whitish-grey color, and of excessively difficult fusion. According to Hielm, its specific gravity is 7.4; according to Bucholz, it is as high as 8.6, and of the color of silver, and somewhat malleable. It is little changed by air, and a conductor of electricity. Its specific heat is 0.07218. (REGNAULT.) When exposed to heat and oxygen, molybdenum is acidified, a white crystalline sublimate of *molybdic acid* being formed. At a lower temperature, it first acquires a brown and then a blue film. It is not acted on by dilute sulphuric, hydrochloric, or hydrofluoric acid; boiled in sulphuric acid, sulphurous acid is evolved, and a brown compound formed: it is dissolved by nitric acid, and very readily by nitrohydrochloric acid. It is rapidly oxidized by fusion with saltpetre, and slowly by fusion with hydrated potassa.

Molybdenum forms three compounds with oxygen, two of which are salifiable, and the third, an acid. Its equivalent number is 48. (47.7 TURNER: 47.96 GRAHAM: 48 GMELIN.)

PROTOXIDE OF MOLYBDENUM. MOLYBDOUS OXIDE. MoO_3 , is obtained

by dissolving molybdic acid, or molybdate of ammonia, potassa, or soda, in aqueous hydrochloric acid, and putting a piece of pure zinc into the solution; the liquid changes to blue, red, and black; excess of ammonia is then added, by which protoxide of molybdenum is thrown down in the form of a *black hydrate*, whilst the oxide of zinc is retained in solution; the hydrate is then washed, and dried in vacuo over sulphuric acid: it is apt to retain adhering oxide of zinc. (BERZELIUS.) Molybdous oxide may be obtained pure by decomposing molybdate of potassa by excess of hydrochloric acid, and agitating the liquid with an amalgam of potassium (containing little potassium); when it has acquired a black color ammonia is added, which throws down the hydrated oxide. (DUMAS.) When fused or crystallized molybdic acid is long digested with zinc and hydrochloric acid, it is not dissolved, but gradually converted into anhydrous protoxide: but exposed in this state to the air it becomes purple and blue by absorbing oxygen. (BERZELIUS.)

In the state of hydrate this oxide is soluble in the acids, but when anhydrous almost insoluble; it is also insoluble in the caustic and carbonated alkalis, but the recently-precipitated hydrate is soluble in carbonate of ammonia. Molybdous oxide consists of

						Berzelius.
Molybdenum	1	48	85.7 85.69
Oxygen	1	8	14.3 14.31
<hr/>						<hr/>
Protoxide of molybdenum	1		56		100.0	100.00

BINOXIDE OF MOLYBDENUM. DEUTOXIDE OF MOLYBDENUM. MOLYBDIC OXIDE. MoO_2 . This oxide was obtained by Bucholz, by strongly heating *molybdate of ammonia* rammed down in a crucible: the molybdic acid is reduced by the hydrogen of the ammonia, and a crystalline copper-colored binoxide is obtained, of the specific gravity 5.6. It may be best procured, according to Berzelius, by heating a mixture of sal-ammoniac and molybdate of soda in a platinum crucible till the fumes cease: the residue is well washed, digested in caustic potassa to separate any molybdic acid, and again washed with boiling water. The oxide remains in the form of a black powder, becoming dark-brown when dry, and purple when exposed to the sun's rays. When pure protoxide is heated in the air it also burns into binoxide.

Although zinc reduces molybdic acid to the state of protoxide, copper only brings it down to binoxide; if therefore copper, molybdic acid, and hydrochloric acid, are put together, the molybdic acid disappears, and the liquid acquires a deep red tint: it contains the chlorides of copper and molybdenum; by excess of ammonia, the binoxide of molybdenum is thrown down, and the oxide of copper retained in solution; the precipitate is cleansed by washing with solution of ammonia, and when carefully dried in vacuo over sulphuric acid, is the hydrated binoxide.

Hydrated molybdic oxide is brown, but becomes green by exposure; it is slightly soluble in distilled water, but insoluble in saline solutions; it is said to redden litmus, but has no other acid characters, and is insoluble in caustic alkalis, but soluble in the carbonates and bicarbonates. When heated in vacuo it becomes dark brown, and loses its solubility, resembling then the anhydrous oxide obtained as above. Molybdic oxide consists of

						Bucholz.	Berzelius.		
Molybdenum	1	...	48	...	75	...	73	...	75
Oxygen	2	...	16	...	25	...	27	...	25
<hr/>									
Deutoxide of molybdenum.....	1		64		100		100		100

MOLYBDOUS ACID. When metallic molybdenum and molybdic acid are boiled together in water, a blue solution is formed, which has sometimes been termed *molybdous acid*, and regarded as a distinct stage of oxidizement, but which appears to be a compound of molybdic acid with the binoxide, and consequently a *molybdate of oxide of molybdenum*. When a current of hydrogen gas is passed over molybdic acid at a dull red-heat, it acquires a blue color, and becomes converted into molybdous acid. This compound is soluble in water, and yields a rich blue solution, which becomes quite colorless on moderate dilution; it is insoluble in solution of sal-ammoniac; it is immediately converted into molybdic acid by nitric acid, nitrohydrochloric acid, and chlorine; and on the other hand, deoxidizing agents, such as protochloride of tin, or tin-filings and hydrochloric acid, convert molybdic acid into this blue compound. Its composition has not been accurately determined, but it probably is MoO_2 , MoO_3 .

PEROXIDE OF MOLYBDENUM. MOLYBDIC ACID. MoO_3 . To obtain this acid, the native sulphuret of molybdenum should be roasted and triturated, to reduce it to powder, and distilled, with three or four parts of nitric acid, to dryness. This operation should be repeated, till it is converted into an uniform white mass, which consists of molybdic, nitric, and sulphuric acids; the two latter may be expelled by a red-heat in a platinum crucible, and the remaining molybdic acid repeatedly washed with boiling water, in which it is little soluble, will be nearly pure. It may be rendered perfectly pure by solution in ammonia, precipitation by nitric acid, and exposure to heat. Molybdic acid may also be procured by roasting the powdered native sulphuret at a low red-heat, till it ceases to give out sulphurous acid; the residue, by digestion in ammonia, affords a *molybdate of ammonia*, which may be purified by crystallization, and decomposed by a moderate heat in a platinum crucible, so as to leave the molybdic acid.

Molybdic acid, thus procured, is a white powder, of the specific gravity 3.46, and requiring, according to Hatchett, 960 parts of boiling water for its solution, which is yellow, reddens litmus, but has no sour taste. Its solubility probably differs with its aggregation, for Bucholz found it soluble in about 500 parts of cold water, and others in 570 and 600. Heated to redness in an open vessel, it slowly sublimes, and condenses in brilliant yellowish scales. It dissolves in hot sulphuric acid, forming a solution, which is colorless while hot, but on cooling acquires a blue color, which is heightened by the addition of soda. Its hydrochloric solution is pale yellowish-green, but becomes blue when saturated by potassa. (HATCHETT, *Phil. Trans.*, 1796.)

It dissolves in the alkalis, forming solutions which are colorless, and from which the molybdic acid is at first precipitated, but afterwards dissolved, by the stronger acids. Molybdic acid is composed of

						Berzelius.	Bucholz.		
Molybdenum	1	48	66·7	66·613	67·5
Oxygen	3	24	33·3	33·387	32·5
<hr/>									
Molybdic acid.....	1		72		100·0		100·000		100·0

MOLYBDATE OF AMMONIA. $\text{NH}_4\text{O}, \text{MoO}_3$. This salt is obtained by dissolving molybdic acid in excess of ammonia, and leaving it to spontaneous crystallization; it forms square prisms, of a pungent metallic taste. When the ammoniacal solution is boiled down, it affords, on cooling, a crystalline mass of *bimolybdate* of ammonia, which, by spontaneous evaporation, may be obtained in rhombic crystals of a pale bluish-green color, and difficultly soluble in water. Distilled in close vessels this salt yields water, ammonia, and nitrogen, and leaves brown bin-oxide; in open vessels the residue is molybdic acid. (BERZELIUS.)

MOLYBDATE OF POTASSA. KO, MoO_3 , is formed by digesting the acid in solution of potassa; or by heating to redness 2 parts of nitre with 1 of molybdic acid, and lixiviating the mass. Its solution, which is colorless, yields small rhomboidal crystals by evaporation, and affords a precipitate of molybdic acid, to hydrochloric, nitric, and sulphuric acids. When chlorine is passed through it, a white powder falls, difficult of solution in cold water, but instantly dissolved by hot, which Berzelius suspects to be a *bimolybdate*.

MOLYBDATE OF SODA. NaO, MoO_3 , is more soluble than molybdate of potassa, and furnishes permanent and transparent crystals. In obtaining this salt, a deposit of a yellowish powder ensues, which is probably a *bimolybdate of soda*.

MOLYBDATE OF LIME. CaO, MoO_3 , is thrown down in the form of an insoluble powder, when alkaline molybdates are added to solutions of lime.

MOLYBDATE OF BARYTA. BaO, MoO_3 , falls in the form of a flocculent precipitate, which collects into crystalline grains, when molybdate of ammonia is added to a solution of nitrate of baryta: by heat it acquires a blue tint: it dissolves in nitric and hydrochloric acids, and these solutions deposit it, when evaporated, in the form of a crystalline crust.

MOLYBDATE OF STRONTIA. SrO, MoO_3 , is insoluble in water.

MOLYBDATE OF MAGNESIA. MgO, MoO_3 , is soluble in water, and forms clusters of small prismatic crystals, which become yellow when heated, and lose 28 *per cent.* of water: it dissolves in 12 to 15 times its weight of water. (BERZELIUS.)

MOLYBDATE OF MANGANESE. MnO, MoO_3 , is a brownish-white and somewhat soluble powder. (RICHTER.)

MOLYBDATE OF PROTOXIDE OF IRON is insoluble, and of a dark-brown color. (SCHEELE.)

MOLYBDATE OF PEROXIDE OF IRON is a yellowish-brown precipitate, decomposed by caustic alkali.

MOLYBDATE OF ZINC is insoluble in water, white, pulverulent, and soluble in the stronger acids. It is obtained by mixing the solutions of molybdate of ammonia and sulphate of zinc. (BRANDES.)

MOLYBDATE OF PEROXIDE OF TIN is a grey powder, insoluble in water, soluble in caustic potassa and in hydrochloric acid, but not altered by nitric acid. (BERZELIUS.)

MOLYBDATE OF CADMIUM. When solutions of molybdate of ammonia and sulphate of cadmium are mixed, a greyish-white powder is thrown down, which when gently ignited becomes brown. (BRANDES.)

MOLYBDATE OF COBALT is precipitated of a dirty-yellow color, but becomes red by drying: it is decomposed by the alkalis and by the stronger acids. (BERZELIUS.)

MOLYBDATE OF NICKEL is a pale-green powder, soluble in boiling water. When molybdic acid is added to nitrate of nickel, a white precipitate falls, provided there is no excess of nitric acid. (HATCHETT.)

MOLYBDATE OF LEAD. PbO, MoO_3 . This compound is precipitated in the form of an insoluble powder, on mixing solutions of molybdate of ammonia and nitrate of lead; it is of a pale-yellow color, and soluble in nitric acid and in caustic alkalis. It occurs *native*, crystallized, and of different shades of yellow; it was first discovered in Carinthia, and has since been found in Mexico, Hungary, and Saxony; its density is 5.7; it was analyzed by Hatchett. (*Phil. Trans.*, 1796, p. 323.) It consists of

					<i>Native.</i>		<i>Artificial.</i>				
					Hatchett.	Göbel.	Berzelius.				
Oxide of lead	1	...	112	...	60·87	...	60·4	...	59·5	...	64·42
Molybdic acid.....	1	...	72	...	39·13	...	39·6	...	40·5	...	35·58
<hr/>											
Molybdate of lead	1		184		100·00		100·0		100·0		100·00

MOLYBDATE OF COPPER is yellow-green, difficultly soluble in water, and easily decomposed by acids and alkalis. (BERZELIUS.)

MOLYBDATE OF URANIUM is a pale-yellow powder, soluble in the stronger acids and in carbonate of ammonia; when heated it becomes blue: it is obtained by adding molybdate of ammonia to persulphate of uranium: it consists of 43.75 molybdic acid + 56.25 peroxide of uranium. (BRANDES.)

PROTOCHLORIDE OF MOLYBDENUM. MoCl . When the vapor of bichloride of molybdenum is passed over molybdenum heated nearly to redness, a deep red compound is obtained, which yields a crystalline sublimate when heated in an open tube: it is insoluble in water, but is decomposed by solution of potassa, yielding pure hydrated protoxide of molybdenum. Berzelius states that the sublimate formed in *vacuo* dissolves in water. This chloride forms double salts with sal-ammoniac, and with chloride of potassium.

BICHLORIDE OF MOLYBDENUM. MoCl_2 . This compound is formed by heating metallic molybdenum in pure and dry chlorine; the metal

burns, and a red vapor fills the retort, which condenses into crystals resembling iodine; they are fusible, volatile, and in the air first fume a little, and then deliquesce into a black liquid, which changes color in proportion to the water it absorbs, becoming blue-green, green-yellow, dark-red, rose-colored, and lastly, yellow. When the crystals are thrown into water, much heat is evolved; if the solution be dilute, it becomes green or blue in consequence of oxidizement. This chloride forms a double *ammonio-chloride of molybdenum* with sal-ammoniac, but does not combine with the chlorides of potassium or sodium. (BERZELIUS.)

PERCHLORIDE OF MOLYBDENUM. When a current of chlorine is passed over gently-heated binoxide of molybdenum, a yellowish crystalline sublimate is formed, and molybdic acid remains in the tube: this compound is less volatile than the bichloride, but it rises in vapor at a temperature below redness: it does not fuse. It readily dissolves in water, and is soluble in alcohol: its taste is sharp, astringent, and afterwards sour. (BERZELIUS.) According to H. Rose (*Ann. Ch. et Ph.*, LXvi. 218), this is a compound of molybdic acid with perchloride of molybdenum = $\text{MoCl}_3, 2\text{MoO}_3$.

IODIDES OF MOLYBDENUM. Iodine has no action on metallic molybdenum at any temperature. *Protiodide of Molybdenum* may be formed by dissolving the protoxide in hydriodic acid. *Biniodide of Molybdenum* is produced when the binoxide is dissolved in hydriodic acid: the solution yields dark red crystals on evaporation.

BROMIDE OF MOLYBDENUM has not been examined.

FLUORIDES OF MOLYBDENUM. *Protofluoride of Molybdenum* is formed by dissolving the hydrated protoxide in hydrofluoric acid; a dark-purple solution is obtained, which by very careful evaporation leaves a purple viscid residue; at a higher temperature it becomes brown, and loses its perfect solubility in water: it forms compounds with ammonia, and with the fluorides of potassium and sodium. *Bifluoride of Molybdenum* is formed by saturating hydrofluoric acid with the binoxide: on evaporation a black crystalline compound is obtained, which yields a red aqueous solution: it forms double salts with ammonia, potassium, and sodium. *Perfluoride of Molybdenum* is the result of the solution of molybdic acid in hydrofluoric acid; it yields, on evaporation, a yellow uncrystallizable residue, which easily acquires a blue tinge from dust, or other reducing agents.

MOLYBDENUM AND SULPHUR. There are three *sulphurets of molybdenum*, two of which correspond with the binoxide and with molybdic acid, and the third contains 4 equivalents of sulphur; no *protosulphuret*, corresponding with the protoxide, has as yet been formed.

BISULPHURET OF MOLYBDENUM, MoS_2 , is produced artificially by intensely heating a mixture of molybdic acid and sulphur, out of the contact of air. It forms the *native sulphuret*, and consists of

						Bucholz.	Brandes.
Molybdenum	1	...	48	...	60	...	59.6
Sulphur	2	...	32	...	40	...	40.4
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Bisulphuret of molybdenum	1		80		100		100.0

Native Sulphuret of Molybdenum is found in Bohemia, Sweden, and near Mont Blanc, disseminated in a grey granite. It also occurs in England, chiefly in Cornwall; and in Scotland, in Inverness-shire. Its sp. gr. is about 4.25. It is found exclusively in primitive rocks; generally in granite, and with quartz: it rarely occurs crystallized; generally massive, and in easily-separable laminae: it is soft and unctuous to the touch, and in color much like lead; infusible, and unchanged by heat when air is excluded. Digested in nitrohydrochloric acid it yields molybdic and sulphuric acids: boiled with sulphuric acid, sulphurous acid is evolved, and a blue solution formed: nitric acid oxidizes without dissolving it.

TERSULPHURET OF MOLYBDENUM, MoS_3 , is obtained by saturating a strong solution of a molybdic salt with sulphuretted hydrogen, and then adding hydrochloric acid; a dark-brown precipitate falls, which becomes black on drying, and which, when heated in close vessels, gives off sulphur, and becomes bisulphuret: it dissolves slowly in the caustic alkalis, and more easily in the alkaline hydrosulphurets. It consists of

						Berzelius.
Molybdenum	1	...	48	...	50	49.72
Sulphur	3	...	48	...	50	50.28
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Tersulphuret of molybdenum	1		96		100	100.00

This sulphuret combines with the sulphurets of the electro-positive metals (alkaline bases), and forms a class of *sulphur-salts*, which may be called *molybdo-tersulphurets*. The *Molybdo-tersulphuret of Potassium*, KS,MoS_3 , is formed by saturating molybdate of potassa by sulphuretted hydrogen, and evaporating; it forms prismatic crystals of a beautiful green and iridescent lustre: by transmitted light they are ruby red, soluble in water, and insoluble in alcohol; on the addition of the stronger acids, sulphuretted hydrogen is evolved, tersulphuret of molybdenum is precipitated, and a salt of potassa remains in solution. This salt is anhydrous, and consists of

						Berzelius.
Sulphuret of potassium	1	...	56	...	36.8	35.57
Tersulphuret of molybdenum	1	...	96	...	63.2	64.43
<hr/>						
Molybdo-tersulphuret of potassium	1		152		100.0	100.00

Similar soluble *molybdo-tersulphurets* may be formed with sulphurets of sodium and lithium, and with those of barium, strontium, and calcium; and several insoluble *molybdo-tersulphurets* are obtained by double decomposition. (BERZELIUS.)

PERSULPHURET OF MOLYBDENUM. QUADRISULPHURET OF MOLYBDENUM. MoS_4 . This compound is obtained as follows: saturate bimolybdate of potassa with sulphuretted hydrogen, and boil the resulting turbid solution for some hours in a retort; when it cools, a black light powder, and red crystalline scales, are deposited, which must be separated as far as possible; the red crystalline deposit is then washed upon a filter with water, till the washings no longer afford a *red* (not a brown) precipitate with hydrochloric acid; the residue upon the filter is then treated by boiling water, and the dark-red solution which filters through is

decomposed by excess of hydrochloric acid; a bulky dark-red or brown precipitate falls, which, when washed and dried, shrinks, acquiring a grey lustre, and giving a cinnamon-brown powder. It consists of

						Berzelius.
Molybdenum.....	1	...	48	...	42·36	42·58
Sulphur	4	...	64	...	57·14	57·42
<hr/>						<hr/>
Persulphuret of molybdenum	1		112		100·00	100·00

This, like the tersulphuret, combines with the protosulphurets of the electro-positive metals, and forms *molybdo-persulphurets*; they are rarely crystallizable, and have a red or orange color.

SALTS OF THE OXIDES OF MOLYBDENUM. There are three classes of these salts; those of the *protoxide*; of the *binoxide*; and of *molybdic acid*.

1. The salts of the *protoxide* are black or deep purple; they have a purely astringent taste. 2. The salts of the *binoxide*, when anhydrous, are nearly black, but red when they contain water of crystallization: their solutions have an astringent, sourish, and metallic taste; they are rendered brown by infusion of galls, and a grey-brown precipitate falls; ferrocyanide of potassium occasions a dark-brown precipitate, which is insoluble in excess of the precipitant. They are rendered black by an immersed plate of zinc, and a black zinciferous protoxide of molybdenum falls. 3. The *molybdic acid*, before it has been heated, is soluble in the other acids, and produces a class of compounds which, in some of their characters, resemble salts; but they combine with the alkalis in the manner of a double acid.

There is also a class of molybdic compounds of a deep-blue color; they are double salts, the basis of which is a compound of the binoxide with molybdic acid; the *sulphate* thus formed is deep-blue, but becomes quite colorless when diluted with 3 or 4 parts of water.

Before the blow-pipe molybdic acid melts upon charcoal with ebullition, and is absorbed. In a platinum spoon it emits white fumes, and is reduced in the interior flame to molybdic oxide, which is blue, but in the exterior flame it is again oxidated and becomes white. With microcosmic salt, in the exterior flame, a small proportion of the acid gives a green glass, which by gradual additions of the acid passes through yellow-green to reddish, brownish, and hyacinth-brown, with a slight tinge of green. In the interior flame the color passes from yellow-green, through yellow-brown, and brown-red, to black; and if the proportion of acid be large, it acquires a metallic lustre, like the sulphuret, which sometimes remains after the glass has cooled. Molybdic acid is but sparingly dissolved by borax. In the exterior flame the glass acquires a grey-yellow color. In the interior flame black particles are precipitated from the clear glass, leaving it almost colorless when the quantity of molybdenum is small, and blackish when the proportion is large. If, to a glass formed of this acid and microcosmic salt, a little borax be added, and the mixture fused in the exterior flame, the color becomes instantly reddish-brown: in the interior flame the black particles are also separated, but in smaller quantity. By long-continued heat the color of the glass is diminished, and it appears yellower by the light of a lamp than by day-light. This acid is not reduced by soda in the interior flame.

§ XXVI. CHROMIUM. Cr. 28.

CHROMIUM was discovered by Vauquelin in 1797. It was named from *χρῶμα*, *color*, on account of its tendency to produce colored compounds. Its two native combinations are the *chromate of lead*, in which the metal was originally discovered (*Ann. de Ch.*, xxv. and lxx.), and the *chromite of iron*, which is a compound of the oxides of chromium and iron, found abundantly at Unst, in Shetland, and in several parts of Europe and America. It also occurs in small proportion as the coloring matter of several minerals.

Metallic chromium may be obtained by intensely igniting its *oxide* with about a tenth of its weight of charcoal, but the reduction is difficult and imperfect. According to Dumas the color of chromium resembles that of platinum; it scratches glass, and takes a good polish; he could not succeed in fusing it into a button, but only obtained it in a spongy mass superficially fused, though the furnace which he employed was adequate to the fusion of a pound of soft iron in fifteen minutes. When pure it is not magnetic. Its density is 5.9. The properties of chromium vary much with its state of aggregation, it being susceptible of what Berzelius terms two allotropic conditions: obtained in a finely divided state by the action of potassium on sublimed chloride of chromium, the metal is pulverulent, burns when gently heated into green oxide, and is energetically acted on by most of the acids: whereas when obtained by the usual modes of reduction, it is comparatively indifferent to the action of powerful reagents. The equivalent of chromium may be assumed as 28.

CHROMIUM AND OXYGEN. According to Peligot, there are five oxides of chromium, which he represents as isomorphous with the corresponding oxides of iron, (*Ann. Ch. et Ph.*, Dec. 1844), namely, (1.) *Protoxide*, CrO . (2.) *Deutoxide*, Cr_3O_4 . (3.) *Binoxide*, CrO_2 , which may also be regarded as a chromate of the sesquioxide, or as $\text{Cr}_2\text{O}_3, \text{CrO}_3$. (4.) *Sesquioxide*, Cr_2O_3 . (5.) *Chromic Acid*, CrO_3 .

PROTOXIDE OF CHROMIUM, CrO , is obtained in the form of a brown hydrate by the action of potassa on the corresponding *protochloride*: it is extremely unstable, and passes by the action of air into the above-mentioned *deutoxide*, which is isomorphous with the magnetic oxide of iron.

SESQUIOXIDE OF CHROMIUM. Cr_2O_3 . (*Green oxide* or *protoxide* of several authors.) There are several modes of obtaining this oxide: (1.) When metallic chromium, in a finely divided state, is exposed to the action of heat and air, it combines with oxygen, and this oxide is formed. When steam is passed over the metal at a red-heat, hydrogen is evolved, and the green sesquioxide formed. (2.) When *chromate of mercury* is heated to redness, mercury and oxygen are given off, and a pure green oxide remains. (3.) It may be obtained by calcining a mixture of equal parts of *chromate of potassa* and sulphur in a close earthen crucible, at a red-heat, and washing the green mass which is produced, to dissolve out the sulphate and sulphuret of potassium; the oxide of chromium remains,

and is rendered pure by repeated washings. (*Ann. Ch. et Ph.*, xiv. 299.) (4.) By digesting chromate of lead in a mixture of hydrochloric acid and alcohol, chloride of lead is thrown down, and sesquichloride of chromium remains in solution; it may be precipitated in the state of *carbonate of chromium* by carbonate of potassa, and this precipitate washed, and heated red-hot, yields the pure sesquioxide. (5.) Chromate of potassa may be dissolved in excess of hydrochloric acid, and sulphuretted hydrogen passed through the solution, which reduces the chromic acid to oxide, the hydrochloric solution of which may be decomposed as above. (6.) Chromate of potassa may be boiled with hydrochloric acid and alcohol, by which, as in the case of chromate of lead, a solution of sesquichloride of chromium is obtained: the oxide may then be thrown down either by ammonia or by an alkaline carbonate, and the resulting hydrate or carbonate may be reduced to the state of pure oxide by calcination. (7.) When chromate of lead is heated in a crucible coated with charcoal, oxide of chromium and metallic lead are obtained: they may be separated by triturating the mass and sifting it, when the lead remains upon the sieve. (8.) A mixture of equal parts of bichromate of potassa and sal-ammoniac, when calcined, yields a green mass, which, when well washed, leaves sesquioxide of chromium: in this case $\text{KO}, 2\text{CrO}_3 + \text{NH}_4\text{Cl} = \text{Cr}_2\text{O}_3, \text{KCl}, 4\text{HO}, \text{N}$. (9.) When the vapor of chlorochromic acid is passed through a white-hot tube, chlorine and oxygen are disengaged, and the tube becomes lined with crystals of sesquioxide of chromium: $2 [\text{CrO}_3, \text{Cl}]$ give $\text{Cr}_2\text{O}_3, 2\text{Cl}, 3\text{O}$. These crystals are of so deep a green as to appear nearly black; their lustre is metallic, and they are so hard as to scratch glass; their density is 5.21. (WÖHLER.) Sesquioxide of chromium is of a green color, the shades of which are deeper in proportion to the temperature to which it has been exposed; it is infusible and unchanged by heat. When obtained by gently drying the hydrate, and heated nearly red-hot in a crucible, it suddenly becomes ignited throughout, without either gaining or losing weight: this occurs in close as well as in open vessels; when cool it has a fine green color, and has become insoluble in the acids. To render it again soluble, it must be digested in concentrated sulphuric acid, or fused with caustic potassa, or with nitre. In this respect it resembles zirconia and titanous acid. It is converted into *chromic acid* by deflagration with nitre. Fused with vitrifiable substances, and especially with borax, it confers upon them a characteristic green color: hence its use in porcelain and enamel painting.

Hydrated Sesquioxide of Chromium. When this oxide is precipitated from its acid solutions by the caustic fixed alkalis, it falls in the form of a bulky green powder, slightly soluble in excess of the alkali, but again thrown down on boiling the solution: in this state it is a *hydrate*. It is sparingly dissolved by excess of ammonia, forming a red solution. It may be best obtained by adding a mixture of equal parts of hydrochloric acid and alcohol, in small portions, to a boiling solution of chromate of potassa, until the liquid acquires a pure green color; when cold, excess of ammonia is added, which precipitates the oxide combined with a large relative proportion of water; and in this state it readily dissolves in the acids. (THOMSON.) According to Hertwig, the precipitate formed by ammonia in the solutions of the sesquioxide of chromium is never a pure hydrated oxide, but retains, after having been washed by boiling water, a variable

proportion of ammonia, which may be expelled by potassa: he has described a green and a violet modification of this precipitate. (*Ann. der Pharm.*, XLV. 299.)

When tartaric acid is added to the aqueous solution of *chromate of potassa*, it causes an effervescence, and the solution becomes green in consequence of the conversion of the chromic acid into sesquioxide: the addition of ammonia now throws down a bulky green tasteless powder, readily soluble in acids, which is the hydrated oxide; when heated, it loses as much as thirteen-fifteenths of its weight of water, leaving two-fifteenths of dry oxide, of a green color, but difficultly soluble. According to Thomson, this therefore contains a larger quantity of water than any other metallic hydrate. According to Trommsdorf, this hydrate, dried at 212°, retains 26 *per cent.* of water, and is Cr2 O3,3HO.

The sesquioxide consists of

						Berzelius.
Chromium	2	56	70 70·11
Oxygen	3	24	30 29·89
<hr/>						
Sesquioxide of chromium ...	1		80		100	100·00

Native Sesquioxide of Chromium has been found in France, in the department of the Rhone, in the form of a green incrustation. It is the coloring matter of the emerald, and exists in a few other minerals, such as diallage and some varieties of serpentine. This oxide generally occurs combined or mixed with silica and alumina, the richest specimens containing not more than 13 *per cent.*: their shades of green vary accordingly.

BINOXIDE OF CHROMIUM. CrO2. When nitrate of chromium is decomposed at a dull red-heat, an insoluble *brown binoxide* is formed. When heated with hydrochloric acid, chlorine is evolved. According to Berzelius, when a solution of chromic acid in sulphuric acid is digested with the hydrated green oxide of chromium, a brown solution is obtained, from which the binoxide, in the state of hydrate, is precipitated by the caustic alkalis: he says that it dissolves in, and gives distinct salts with the acids, distinguished from the sesquisalts by their brown color, and convertible into them by deoxidizing agents. At a bright red-heat this oxide loses oxygen, and becomes sesquioxide, so that it is difficult to obtain it pure, for if the nitrate be not adequately heated, the product contains nitric acid; and if overheated, oxide of chromium. According to Döbereiner, this oxide may be regarded as a chromate of the sesquioxide, or Cr2 O3,CrO3.

CHROMIC ACID. PEROXIDE OF CHROMIUM. CrO3. Chromic acid may be procured by the following processes: (1.) Mix 4 parts of chromate of lead with 3 of finely-powdered and pure fluor-spar (previously heated red-hot), and 5 of concentrated sulphuric acid; introduce this mixture into a distillatory apparatus of lead or platinum, and gently heated; a red vapor is liberated, which is conducted into distilled water contained in a vessel of platinum; it is thus condensed into a dark orange-colored liquid; the red vapor is a *fluoride of chromium*, and is resolved by water into hydrofluoric and chromic acids, the solution of which, evapo-

rated in a platinum vessel, leaves pure chromic acid. If, instead of conducting the vapor into water, it be received into a platinum vessel, containing pieces of moist blotting-paper, it is decomposed as before, but the chromic acid is deposited in beautiful silky acicular crystals, which soon deliquesce. (UNVERDORBEN.) (2.) Decompose a hot concentrated solution of bichromate of potassa by fluosilicic acid: the chromic acid, after being separated from the sparingly-soluble fluosilicate of potassium, is evaporated to dryness in a platinum capsule, and then redissolved in the smallest possible quantity of water: by this means the last portions of the fluosilicate are rendered insoluble, and the chromic acid may be separated by decantation. The acid must not be filtered in this concentrated state, as it then corrodes paper like sulphuric acid, and is converted into bin-oxide, or into a chromate of the green oxide. When it is wished to prepare a large quantity of chromic acid by this process, porcelain vessels may be employed in the first part of the operation, provided care be taken to add a quantity of silicated fluoric acid, not quite sufficient for precipitating the whole of the potassa. (MAUS.) (3.) Take 100 measures of a cold saturated solution of bichromate of potassa (prepared by boiling, and then allowing the solution to cool and deposit its excess of salt), and add to this from 120 to 150 measures of concentrated sulphuric acid (free from lead). The mixture, on cooling, gradually deposits dark crimson needles of chromic acid: decant, and place the crystals on a thick flat tile of biscuit porcelain; another tile is then to be placed on the crystals, and the whole submitted to pressure for a considerable time. On removing the chromic acid, it will be found dry, and retaining scarcely a trace of sulphuric acid. (WARINGTON.) (4.) According to Schrötter, the acid obtained by Warington's process retains from 6 to 7 *per cent.* of potassa, and 0·7 of sulphuric acid; he gives the following as yielding a purer acid: 2 parts of concentrated sulphuric acid are added to 1 of dry chromate of lead, and in about twelve hours the decomposition is complete, and on adding water sulphate of lead remains, and a red solution of chromic, with some sulphuric acid, is obtained, which is evaporated in a retort, and on cooling crystals of chromic acid are deposited, which, when dried on absorptive tiles, only retain about 1·2 *per cent.* of sulphuric acid, not chemically combined. (*Chem. Gaz.*, Oct. 1843.) (5.) Balmain obtains chromic acid by decomposing chromate of mercury or of silver by an equivalent of hydrochloric acid. (*Chem. Gaz.*, Nov. 1843.)

Chromic acid is of a scarlet color, becoming darker when heated; its taste is sour and metallic; it tinges the cuticle yellow; it may be obtained from its aqueous solution in deliquescent but anhydrous prismatic crystals, of a ruby color: heated to redness it gives out oxygen, and leaves sesquioxide; it is energetically acted on and converted into oxide by ammonia. It dissolves in alcohol, and the solution gradually deposits green oxide. It is a powerful oxidizing and bleaching agent, yielding half its oxygen to oxidizable bodies, and being reduced to sesquioxide, $2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + \text{O}_3$: hence a mixture of bichromate of potassa and sulphuric acid is frequently resorted to as a means of oxidizing organic bodies. The aqueous solution of chromic acid is decomposed by the sun's rays, and deposits the oxide. Chromic acid appears to be the coloring matter of the ruby. In combination with oxide of tin it forms a pink color used in porcelain painting. (*Ann. Ch. et. Ph.*, Lxi. 433.) The salts of chromic

acid are said to be isomorphous with those of the sulphuric and selenic acids. This acid is composed of

						Berzelius.
Chromium.....	1	28	53.85 53.98
Oxygen	3	24	46.15 46.02
<hr/>						<hr/>
Chromic acid.....	1		52		100.00	100.00

CHROMATE OF AMMONIA, $\text{NH}_4\text{O}, \text{CrO}_3$, is formed by saturating ammonia with chromic acid, and concentrating the solution over sulphuric acid in vacuo; it forms yellow crystals, very soluble and having an alkaline reaction. When slowly heated it passes into green oxide; rapidly heated this change ensues with ignition.

BICHROMATE OF AMMONIA is produced when the solution of the preceding salt is concentrated on a sand-heat; it forms red crystalline plates, resulting from an oblique rhombic prism (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 287), and which include 3 atoms of water. (THOMSON.) When heated below redness it is decomposed with slight deflagration.

CHROMATE OF POTASSA. KO, CrO_3 . This salt is prepared by exposing a mixture of 4 parts of powdered native chromite of iron with 1 of nitre, to a strong heat for some hours, and washing out the resulting soluble matter: the process is repeated till the ore is decomposed. The washings yield *chromate of potassa* by evaporation. Dumas directs equal parts of nitre and of the pulverized ore to be heated gradually to redness; by which chromate, silicate, aluminate, and sometimes manganesate of potassa, are produced, forming a porous mass: the oxide of iron is set free; the chromate of potassa is washed out, and the residue, which still contains chromium, may be digested in dilute hydrochloric acid, which dissolves the oxide of iron and alumina, and again heated with nitre. The washings are to be exactly neutralized by nitric acid, which separates the alumina and silica on evaporation; the crystals of chromate are then separated from those of nitrate of potassa, and purified by recrystallization. Dumas observes that the chromates might be abundantly obtained at a moderate price if the American chromates of iron were decomposed there by the nitrate of soda of Peru. According to Nasse the decomposition of the native chromite is more perfectly effected by heating a mixture of 3 parts of it in fine powder with 4 of nitre and 2 of tartar: the fused mass should be kept at a red-heat for three hours, pulverized and lixiviated; the residue being again similarly treated. Chromate of potassa is often prepared by neutralizing the commercial bichromate with carbonate of potassa.

Chromate of potassa forms yellow crystals, the primary form of which is a right rhombic prism. (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 120.) It has a disagreeable metallic taste. It is extremely soluble in boiling water. At 60° , 100 parts of water dissolve about 48 of the salt. It is insoluble in alcohol. Its specific gravity is 2.6 to 2.7. It is anhydrous: its coloring power is so great, that 1 part gives color to 40,000 of water. (THOMSON.) If 1 grain be dissolved with 20 of nitre, and the solution evaporated, the crystals of nitre are almost as yellow as those of the chromate. When heated to 400° , it acquires a crimson color, but be-

comes again yellow on cooling. When fused, it crystallizes on cooling, but is not decomposed except in contact of carbonaceous matter, when carbonate of potassa and oxide of chromium are produced. When chlorine is passed over chromate of potassa at a red-heat, in a porcelain tube, chloride of potassium and oxide of chromium are formed: the latter crystallized in brilliant laminæ of a green or brown color, dependant upon temperature. When the salt is mixed with charcoal and exposed to the action of chlorine at a high temperature, anhydrous chloride of chromium volatilizes, and a crystalline rose-colored salt remains, which is a double chloride of chromium and potassium. (FREMY, *Journ. de Pharm.*, Feb., 1844.) Heated with acetic acid and alcohol chromate of potassa is converted into acetate of potassa, and acetate of oxide of chromium. (TASSAERT, *Ann. Ch. et Ph.*, xxii. 51.) As it occurs in commerce it is sometimes mixed with sulphate of potassa; the adulteration may be detected by acidulating the solution of the chromate with nitric acid, and testing by nitrate of baryta, when insoluble sulphate of baryta falls. If the chromate be mixed with chloride of potassium, the same acidulated solution will yield a white insoluble precipitate with nitrate of silver.

When solutions of chromate of potassa and protosulphate of manganese are mixed, the fluids become of a deep orange-red color, and a dark brown crystalline film and deposit is gradually formed, consisting of 1 atom of chromic acid, 2 of protoxide of manganese, 2 water. (WARINGTON, *Mem. Ch. Soc.*, March, 1842.)

Chromate of potassa consists of

				Tassaert.	Thomson.
Potassa	1	48	48
Chromic acid	1	52	52
<hr/>					
Chromate of potassa	1		100		100

BICHRIMATE OF POTASSA, $\text{KO}, 2\text{CrO}_3$, is obtained by adding a sufficiency of sulphuric or other acid to a solution of the chromate to give it a sour taste, and setting it aside for a day or two, when deep orange-colored or red crystals are deposited; the acid abstracts half the potassa, and if sulphuric acid be used, there is some difficulty in separating the sulphate from the chromate; nitric acid is preferable, but the purest salt is obtained when acetic acid is used. The crystals are in the form of anhydrous quadrangular prisms and tables, permanent in the air, of a cooling metallic taste, soluble in 10 parts of water at 60° , and much more soluble in boiling water. Their specific gravity is 1.98, THOMSON; 2.6, KARSTEN. At a red-heat, they fuse, without decomposition, into a transparent red liquid, which congeals into a crystalline mass on cooling, and then falls to powder from the unequal contraction of the crystals. At a white-heat, half the acid of the salt is decomposed, forming a mixture of oxide of chromium and neutral chromate of potassa. This salt is largely manufactured at Glasgow, for the use of calico-printers. A solution of it, acidulated by sulphuric acid, has been employed by Warington as an oxidizing agent in Voltaic arrangements. (*Proc. Chem. Soc.*, Part 2, 1841.) When 3 parts of bichromate of potassa are gently heated with 4 of sulphuric acid, potassio-sulphate of chromium is formed and oxygen evolved. $\text{KO}, 2\text{CrO}_3 + 4[\text{SO}_3, \text{HO}] = [\text{KO}, \text{SO}_3 + \text{Cr}_2\text{O}_3, 3\text{SO}_3] + 4\text{HO} + 3\text{O}$. (BALMAIN.) Both the chromate and bichromate of

potassa have a very deleterious action on the system when their solutions are brought much in contact with the skin, causing sores which are painful and difficult to heal. Paper impregnated with these salts and dried, forms excellent tinder. The solutions have powerful antiseptic properties. (GREGORY.) Bichromate of potassa consists of

						Grouvelle.	Thomson.	Tassaert.			
Potassa	1	...	48	...	31·6	...	31·154	...	31·579	...	32·6
Chromic acid	2	...	104	...	68·4	...	68·846	...	68·421	...	67·4
<hr/>											
Bichromate of potassa	1		152		100·0		100·000		100·000		100·0

TERCHROMATE OF POTASSA, KO_3CrO_3 , is obtained in crystals by evaporating a mixture of the solution of the bichromate with nitric acid. (GRAHAM.)

BICHROMATE OF CHLORIDE OF POTASSIUM. KCl_2CrO_3 . When 2 atoms of chromic acid and 1 of chloride of potassium are dissolved in hydrochloric acid, crystals may be obtained from the solution in the form of flat quadrangular prisms, having the color of the bichromate of potassa. The same salt is formed when a solution of bichromate of potassa in hydrochloric acid is boiled; in that case, the requisite chloride of potassium is formed at the expense of the hydrochloric acid and potassa. This salt is permanent in the air, and may be dissolved without decomposition in dilute hydrochloric acid; but by pure water it is again resolved into hydrochloric acid and bichromate of potassa. In this compound, therefore, the chloride of potassium acts as a *base* to the chromic acid. Peligot has obtained similar bichromates of the chlorides of sodium, calcium, magnesium, and ammonium, but could not form them with the chloride of barium or of strontium. (*Ann. Ch. et Ph.*, Lii. 267.) The chlorobichromate of potassium consists of

						Peligot.
Chromic acid.....	2	104	57·8 58·21
Chloride of potassium	1	76	42·2 41·29
<hr/>						
Chromochloride of potassium	1		180		100·0	99·50

CHROMATE OF SODA, NaO,CrO_3 , is obtained by heating to redness a mixture of pulverized chromite of iron with half its weight of caustic soda, and a portion of nitrate of soda: the fused mass is lixiviated with water and the solution filtered and evaporated to form crystals: the salt may also be obtained by fusing a mixture of 1 part of sesquioxide of chromium and 2 of nitrate of soda. It crystallizes in oblique rhombic prisms (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 287), and of a fine yellow color, very soluble in water, and sparingly so in alcohol. They contain 10 atoms of water; but may also be obtained anhydrous. The hydrated crystals effloresce in dry air.

BICHROMATE OF SODA, NaO_2CrO_3 , is more soluble than the preceding: it forms small six-sided prisms, (MOSER:) large irregular plates. (THOMSON.)

CHROMATE OF LITHIA, LO,CrO_3 , forms yellow oblique prisms and arborescent crystals very soluble in water. (C. GMELIN.)

CHROMATE OF LIME. CaO, CrO_3 . When chromate of potassa is mixed with solution of chloride of calcium, a yellow precipitate gradually falls; the salt described by Vauquelin as forming silky crystals, is probably a *bichromate of lime*.

CHROMATE OF BARYTA, BaO, CrO_3 , is a pale yellow powder which falls when chromate of potassa is dropped into chloride of barium: it is as insoluble in water as sulphate of baryta, (J. D. SMITH, *Phil. Mag.*, vi. 280,) but it dissolves, as *bichromate*, in nitric and hydrochloric acid, and in excess of chromic acid, and is again precipitable by ammonia. It consists of

						Vauquelin.	Berzelius.
Baryta.....	1	77	59·7 57·75 59·85
Chromic acid	1	52	40·3 42·25 40·15
<hr/>							
Chromate of baryta	1		129		100·0	100·00	100·00

CHROMATE OF STRONTIA. SrO, CrO_3 . This salt is precipitated in the form of an insoluble yellow powder on mixing solutions of chromate of potassa and nitrate of strontia: it is anhydrous: it dissolves in nitric, hydrochloric, and chromic acids. (GMELIN.)

CHROMATE OF MAGNESIA, MgO, CrO_3 , may be formed by dissolving magnesia in aqueous chromic acid; it forms transparent rhomboidal crystals, very soluble in water, and containing 1 atom of anhydrous chromate + 2 atoms of water. (THOMSON.) According to Graham, the crystals of this salt contain 5HO. “It does not form a double salt with chromate of potassa as sulphate of magnesia does with sulphate of potassa. It is remarked that the insoluble metallic chromates generally carry down portions of the neutral precipitating salts or of subsalts, and their analysis is often unsatisfactory from that cause. When the magnesian chromates are compared with the sulphates of the same family, the former are found to have their water readily replaced by metallic oxides, but not by salts, so that subchromates with excess of oxide are numerous, while few, or no, double chromates exist.”

CHROMATES OF MANGANESE. Neither chromate nor bichromate of potassa produce any immediate precipitate in solutions of the protoxide of manganese, but after a time a brown precipitate falls, which is crystalline when the solutions are dilute, and appears under the microscope in dark-brown acicular groups = $2\text{MnO}, \text{CrO}_3, 2\text{HO}$: they are therefore a *dichromate*: they form a yellow solution in dilute nitric and sulphuric acids. (WARINGTON, *Phil. Mag.*, xxi. 380.) Dried at 212° , they consist of

						Warington.	Reinsch.
Protoxide of manganese	2	72	50·71 51·07 50·9
Chromic acid	1	52	36·62 36·71 37·3
Water	2	18	12·67 12·20 11·8
<hr/>							
Crystallized dichromate of manganese	1		142		100 00	99·98	100·0

Carbonate of manganese is soluble in chromic acid; the solution is

brown, and has an austere metallic taste; it is uncrystallizable, and decomposed by evaporation, a black powder being deposited, which is a chromite of sesquioxide of manganese. (DUMAS.)

CHROMATE OF IRON. No combination of the protoxide of iron with chromic acid can exist, because it abstracts oxygen from that acid, and produces oxide of chromium. The chromate of the peroxide of iron (*perchromate*) is soluble: and there is a brown insoluble subchromate.

The so-called *Native chromate of iron*, is a compound of oxide of chromium with protoxide of iron. There appear to be two chemical varieties of this mineral; one, from the department of the Var, in France, which occurs in blackish-brown amorphous masses, of a slightly metallic lustre, scratches glass, does not affect the magnet, and has a specific gravity of 4.03; it appears to be a compound of 2 atoms of protoxide of chromium, and 1 of protoxide of iron; $2\text{Cr}_2\text{O}_3 + \text{FeO}$; another, from Baltimore and Siberia, massive, or granular, and imbedded in steatite, grey, of the lustre of anthracite, is composed of 3 atoms of oxide of chromium and 2 protoxide of iron. The following analyses are from Dumas. (*Chim. app. aux Arts*, III. 447.)

	Var.		Silesia.		Baltimore.		Oural.		Styria.
Oxide of chromium	37	...	32.3	...	51.6	...	53.0	...	55.5
Oxide of iron.....	35	...	41.0	...	35.0	...	34.0	...	33.0
Alumina	21	...	16.0	...	10.0	...	11.0	...	6.0
Silica	2	...	8.0	...	3.0	...	1.0	...	2.0
	95		97.3		99.6		99.0		96.5

According to Abich the octohedral and massive chromic iron of Baltimore contains magnesia. (*Poggend.*, xxiii. 335.) Gmelin gives the following table of their composition, representing the crystals by the the formula $[\text{5MgO}, \text{8FeO}, \text{10Cr}_2\text{O}_3, \text{3Al}_2\text{O}_3]$.

	Crystallized.	Massive.
Magnesia.....	7.49	9.46
Protoxide of iron	20.99	18.61
Sesquioxide of chromium	59.96	56.74
Alumina.....	11.56	15.19
	100.00	100.00

CHROMATE OF ZINC. Chromate of potassa throws down a yellow flocculent precipitate in solution of sulphate of zinc, soluble in excess of the latter salt, and sparingly soluble in water. According to Thomson, this is a *dichromate*; there is also formed at the same time a double sulphate of potassa and zinc. (*Inorg. Chem.*, ii. 617.) When carbonate of zinc is dissolved in aqueous chromic acid, it yields transparent yellow crystals, isomorphous with sulphate of zinc: they are easily soluble in water: their formula is $\text{ZnO}, \text{CrO}_3, 7\text{HO}$. (KOPP, *Ann. der Pharm.*, xlii. 98.)

CHROMATE OF TIN. Protoxide of tin decomposes chromic acid. *Perchromate of tin* is thrown down as a yellow precipitate when perchloride of tin is mixed with chromate of potassa.

CHROMATE OF CADMIUM may be obtained by mixing solutions of sulphate of cadmium and chromate of potassa; it falls in the state of a beautiful yellow powder which has little or no taste, and yet is not absolutely insoluble in water: it consists of 1 atom of chromic acid + 1 of oxide of cadmium + 5 of water. (THOMSON.) The temperature at which this hydrated salt was dried is not stated.

CHROMATE OF COBALT is a grey or brownish insoluble powder, precipitated on mixing solutions of chromate of potassa and nitrate of cobalt: the fluid remains yellow, so that it is probably a basic salt. (GMELIN.)

CHROMATE OF NICKEL is a red deliquescent salt; the alkalis throw down from it a *subchromate* of an orange color. (BERZELIUS.) When solutions of chromate of potassa and sulphate of nickel are mixed together, no precipitate appears at first, but a reddish-brown powder gradually falls, the quantity of which is increased by concentrating the liquid; when washed and dried, it is a rather beautiful reddish-brown powder, destitute of taste, and not affecting vegetable blues: its constituents are 1 atom of chromic acid + 1 of protoxide of nickel + 4 of water. (THOMSON.)

CHROMATE OF COPPER. When solutions of chromate of potassa and sulphate or chloride of copper are mixed, a buff-colored precipitate falls: it is soluble in ammonia, with a fine green color. It has a slightly sweet taste, and is sparingly soluble in water; it consists, according to Thomson, of 1 atom of chromic acid + 1 of oxide of copper + 2 of water.

When ammonia is gradually added to a mixed solution of 2 parts of sulphate of copper and 1 of bichromate of potassa, heated to between 70° and 80° till the first-formed brown precipitate becomes green, it affords, when carefully dried, a bright-green pigment; but if a proper temperature, and the due quantity of ammonia be not observed, the precipitate loses its chromic acid on washing, and becomes blue hydrated oxide of copper. (LEYKAUF.) Bichromate of potassa occasions no precipitate in solutions of the salts of copper; but when hydrated oxide of copper is dissolved in chromic acid, green crystals of the form of sulphate of copper are obtained on evaporation, containing 33.5 per cent. of water: they are insoluble in alcohol. (KOPP, *Ann. der Pharm.*, xlii. 93.) Gmelin failed in obtaining this salt.

Ammonio-chromate of copper. The solution of chromate of copper in ammonia is of a fine green color: when alcohol is added to it, a dark-green powder falls, which is resolved by boiling water into chromate of ammonia and a pale-green powder, which is a basic double salt. (BÖTTGER.)

CHROMATE OF LEAD. PbO, CrO_3 . When chromate of potassa is added to any of the soluble salts of lead, a fine yellow powder falls, which is the neutral chromate: this salt is generally represented as anhydrous, but when prepared by mixing equivalents of chromate of potassa and acetate of lead in cold solution, the pale yellow precipitate contains an atom of water: when the solutions are hot, the precipitate is deeper-colored and anhydrous. (ANTHON. *Chem. Gaz.*, Jan. 1843.) This

salt is insoluble in water, but soluble in nitric acid, and in solution of potassa: solution of carbonate of potassa forms with it carbonate of lead and chromate of potassa: with hydrochloric acid it forms chloride of lead, and a hydrochloric solution of chromic acid: heated in concentrated hydrochloric acid chlorine is evolved, and chloride of lead, and a green solution, containing chloride of chromium, are formed. When this salt is heated its color is deepened, and it fuses at a red-heat. (VAUQUELIN.) If the heat be continued, it evolves about 4 *per cent.* of oxygen gas, and a mixture of subchromate of lead and oxide of chromium remains. $4[\text{PbO}, \text{CrO}_3] = 2[2\text{PbO}, \text{CrO}_3] + \text{Cr}_2\text{O}_3 + 3\text{O}$. When a current of hydrogen is passed over heated chromate of lead, the formation of water commences below redness, and the temperature rises to a red-heat; the salt blackens from the separation of globules of lead which remain mixed with oxide of chromium: $2[\text{PbO}, \text{CrO}_3] + 5\text{H} = 2\text{Pb} + \text{Cr}_2\text{O}_3 + 5\text{HO}$. (MARCHAND.) It is decomposed by sulphuric acid, sulphate of lead is formed, and chromic acid is set free; if the acid be concentrated, sulphate of chromium is formed. A diluted solution of nitrate of lead being added to a very alkaline solution of chromate of potassa, and left at rest for some time, there was found in the mixed solution, small red crystals, which, upon examination, proved to resemble in all their characters the native chromate of lead. (FARADAY.) According to Wöhler, these crystals are dichromate of lead.

Chromate of lead consists of

						Pfaff.	Berzelius.		
						<i>Native.</i>	<i>Native.</i>	<i>Artificial.</i>	
Oxide of lead	1	112	68·29	67·91 68·38 68·147
Chromic acid	1	52	31·71	31·72 31·62 31·853
<hr/>						<hr/>			
Chromate of lead....		1		164		100·00		99·63	100·00 100·000

Native Chromate of Lead is of a deep orange-red color: when pulverized, orange-yellow. It occurs crystallized in many varieties of form, of which the *primitive* is, according to Haüy, an oblique prism: it is somewhat translucent and brittle. Specific gravity 6. Before the blow-pipe it crackles, and melts into a greyish slag. It occurs in the gold mine of Beresof, in Siberia, in a vein traversing gneiss and mica slate; and near the same place in fissures in a sandstone. (W. PHILLIPS.)

DICHROMATE OF LEAD. SUBCHROMATE OF LEAD. $2\text{PbO}, \text{CrO}_3$. This salt was first noticed by Dulong and Grouvelle, in 1812 and 1822, and its composition pointed out by Badams in 1825. (*Ann. of Phil.*, 2nd Series, ix. 303.) It is formed by digesting the neutral chromate in a dilute solution of caustic potassa; or by boiling a mixture of the neutral chromate with two-thirds its weight of oxide of lead, in water: it is an insoluble scarlet-colored powder, which, when digested in acetic acid, loses half its oxide. Liebig and Wöhler prepare it by adding the neutral chromate to fused nitre, and washing the residue. (*Poggend.*, xxi. 580.) It consists of

						Badams.		
Oxide of lead	2	224	81·16	80·98
Chromic acid	1	52	18·84	19·02
<hr/>						<hr/>		
Dichromate of lead		1		276		100·00		100·00

These chromates of lead are valuable pigments, and used both as oil

and water colors, and in calico-printing and dyeing. (LASSAIGNE, *Ann. Ch. et Ph.*, xv. 76.) As they occur in commerce, they are often adulterated with sulphate of lead and sulphate of lime.

The mineral called *Vauquelinite* is a double chromate of lead and copper, having, according to Berzelius, the formula $[2\text{PbO}, \text{CuO}, 3\text{CrO}_3.]$ The dark-red mineral which has been termed *melanochroit*, is, according to Hermann, a *sesquichromate of lead*, $= 3\text{PbO}, 2\text{CrO}_3$. (*Poggend.*, xxviii. 162.)

CHROMATE OF ANTIMONY. Chromate of potassa added to a hydrochloric solution of oxide of antimony forms a brown precipitate, soluble with a green color in excess of the antimonial solution. (THOMSON.)

CHROMATE OF BISMUTH is formed by mixing chromate of potassa with nitrate of bismuth; it is a lemon-colored powder, very sparingly soluble in water, and reddened by solution of potassa. (GROUVELLE.)

CHROMATE OF URANIUM. Chromate of potassa occasions an ochre-yellow precipitate in solution of nitrate of uranium. (MOSER.) Carbonate of uranium dissolved by chromic acid yields small cubic and dendritic crystals. (JOHN.)

CHROMATE OF MOLYBDENUM. When chromic and molybdic acids are dissolved in boiling-water, they form a yellow solution, which yields on evaporation an uncrystallizable residue, with which water forms a brown solution, and leaves a yellow and difficultly-soluble powder. (BERZELIUS.)

CHROMATE OF CHROMIUM. When nitrate of chromium is heated so as to decompose the nitric acid, and the residue again heated with nitric acid to dryness, so as to expel the acid, without, however, attaining a red-heat, a brownish-yellow powder remains, which, according to Vauquelin, is $\text{Cr}_2\text{O}_3 + \text{CrO}_3$. When hydrated oxide or carbonate of chromium is digested in chromic acid, a solution is obtained of a brown color, which is not decomposed by boiling, and which leaves on evaporation a deliquescent resin-like residue, soluble without decomposition in cold alcohol, and not precipitated by carbonic acid. According to Maus, it is $\text{Cr}_2\text{O}_3 + 4\text{CrO}_3$.

PROTOCHLORIDE OF CHROMIUM, CrCl , is obtained, according to Peligot, in the form of minute white silky crystals, when a current of dry chlorine is passed over a mixture of sesquioxide of chromium and charcoal: violet scales of the sesquichloride are at the same time sublimed. It is also formed by passing a current of hydrogen over the sesquichloride at a dull red-heat, when a white crystalline mass remains, which at a higher heat fuses, and on cooling, presents a fibrous texture. It is soluble in water, and if oxygen be excluded, the solution is *blue*, otherwise green. The green solution abundantly dissolves the sesquichloride. (*Comptes Rendus*, Sept., 1844.)

SESQUICHLORIDE OF CHROMIUM, Cr_2Cl_3 , is formed along with the

protochloride in the process just described: it is also obtained by evaporating the hydrochloric solution of the sesquioxide to dryness, and heating the residue intensely in a retort, or in a stream of chlorine; it forms a crystalline pink sublimate, which yields a green solution with water*. This hydrated sesquichloride resembles the solution of the sesquioxide in hydrochloric acid. It consists of

						Berzelius.	Fellenberg.
Chromium	2	...	56	...	34.1	...	35.2
Chlorine	3	...	108	...	65.9	...	64.8
Sesquichloride of chromium	1		164		100.0		100.0

OXICHLORIDE OF CHROMIUM. CHROMATE OF TERCHLORIDE OF CHROMIUM. $\text{CrCl}_3, 2\text{CrO}_3$. This compound was regarded as a terchloride of chromium, till H. Rose discovered the presence of oxygen in it: it is obtained by heating a mixture of chromate of potassa, chloride of sodium, and sulphuric acid, in which case sulphate of potassa and sulphate of soda remain in the retort, and the oxichloride of chromium distils over: $3[\text{KO}, \text{CrO}_3] + 3\text{NaCl} + 6\text{SO}_3 = 3[\text{KO}, \text{SO}_3] + 3[\text{NaO}, \text{SO}_3] + [\text{CrCl}_3, 2\text{CrO}_3]$. It is a fuming liquid of a brilliant deep-red color; it decomposes water, forming chromic and hydrochloric acids: it inflames phosphorus and sulphur. Its specific gravity is 1.71, and its boiling point 248° . (WALTER.) The color of its vapor resembles that of nitrous acid. When passed through a red-hot tube, it is resolved into oxygen, chlorine, and sesquioxide of chromium. $2[\text{CrCl}_3, 2\text{CrO}_3] = 3[\text{Cr}_2\text{O}_3] + \text{O}_3 + \text{Cl}_6$. This compound is regarded by Walter as chromic acid, in which 1 atom of oxygen is replaced by 1 of chlorine; namely, as $= \text{Cr O}_2 \text{Cl}$. (See also Löwel on the chlorides of chromium, *Ann. Ch. et Ph.*, Sept. 1845.)

IODIDE OF CHROMIUM has not been examined. Iodate of soda occasions a blue precipitate of *iodate of chromium* in a solution of the sesquichloride.

BROMIDE OF CHROMIUM. The solution of this salt is green when dilute, brown when concentrated; it has a sweet astringent taste, and yields a difficultly crystallizable and deliquescent residue when evaporated. By the direct action of bromine on chromium, Berthemot obtained a grey-green deliquescent compound. (*Ann. Ch. et Ph.*, LXIV. 383.) *Bromate of chromium* was attempted to be obtained by Rammelsberg, by adding bromate of baryta to sulphate of chromium, but the green filtered solution evolved bromine on evaporation, and a red crystalline deliquescent substance remained, which was chiefly chromic acid. (*Poggend.*, LV. 87.)

FLUORIDE OF CHROMIUM. When sesquioxide of chromium is dissolved in hydrofluoric acid, and evaporated to dryness, a green crystallized salt remains, soluble in water. It forms difficultly-soluble double

* Peligot says that the pink or violet sesquichloride of chromium is entirely insoluble in pure water; that it dissolves in water containing a mere trace of the protochloride; that heat is always then evolved, and

that the green solution which results has all the characters of the green salts of the sesquioxide. (*Ann. Ch. et Ph.*, December, 1844, 535.)

salts with the fluorides of ammonium, potassium and sodium. (BERZELIUS.)

PERFLUORIDE OF CHROMIUM. TERFLUORIDE OF CHROMIUM. CrF_3 . This compound was discovered by Unverdorben in 1824. (TROMMSDORF'S *Jour. der Pharm.*, ix., and *Edin. Journal of Science*, iv.) He obtained it by the process above described, under the head of *chromic acid*, and it is the red vapor there mentioned (p. 944.) In consequence of its powerful action on glass, the gas can only be collected and preserved in vessels of platinum, so that its properties have been but imperfectly studied: it explodes when mixed with ammonia, and it seems doubtful whether it forms compounds with that gas, analogous to the fluoboric and fluosilicic acids. The action of water on this compound has been above adverted to.

If this compound be a terfluoride, CrF_3 , it should contain about 34 per cent. of chromium and 66 of fluorine, but Rose found it to consist of about 24 chromium and 76 fluorine, and therefore regards it as a *pentafluoride* = CrF_5 . Berzelius, however, considers it as a terfluoride mixed with hydrofluoric acid and some oxygen: or perhaps it is an *oxifluoride*, corresponding with the above-described oxichloride.

CHROMIUM AND NITROGEN. When dry ammonia is passed over sesquichloride of chromium heated in a glass tube, a brown powder remains which Liebig regarded as chromium, (*Poggend.*, xxi. 359), but which has been ascertained by Schrötter to be a *nitruret of chromium* = Cr_3N_2 . In its formation 3 atoms of sesquichloride of chromium and 13 of ammonia, produce 2 of nitruret, 9 of sal-ammoniac, and 3 of hydrogen. $3[\text{Cr}_2\text{Cl}_3] + 13\text{NH}_3 = 2\text{Cr}_3\text{N}_2 + 9[\text{NH}_4\text{Cl}] + 3\text{H}$. This substance when heated in oxygen to between 300° and 400° , burns with a red light into sesquioxide of chromium, and nitrogen and some nitrous acid are evolved. It is composed of

						Schrötter.	
Chromium	3	...	84	...	75	...	76.32
Nitrogen	2	...	28	...	25	...	23.68
	<hr/>		<hr/>		<hr/>		<hr/>
	1		112		100		100.00

NITRATE OF CHROMIUM. When hydrated sesquioxide of chromium is dissolved in nitric acid, the solution is blue by reflected, but red by transmitted light: evaporated to dryness, a red deliquescent uncrystallizable salt remains. A solution of chromic acid in nitric acid yields on evaporation dark brownish-red granular crystals.

SESQUISULPHURET OF CHROMIUM, Cr_2S_3 , is formed by passing the vapor of sulphuret of carbon through a red-hot porcelain tube containing protoxide of chromium; or by heating a mixture of hydrated protoxide and sulphur, in vacuo: it is of a dark-grey color, and when heated in the air it burns into oxide, evolving sulphurous acid: nitrohydrochloric acid converts it into a sulphate of the protochloride of chromium. It is insoluble in potassa and in sulphuret of potassium. This sulphuret is a weak *sulphur base*, and forms a few sulphur salts. It consists of

						Rose and Berzelius.
Chromium	2	56	53·85 54
Sulphur	3	48	46·15 46
<hr/>						
Sulphuret of chromium.....	1		104		100·00	100

SULPHITE OF CHROMIUM. Sulphurous acid readily dissolves the hydrated sesquioxide, and when the solution is boiled a green granular basic sulphite is deposited. (BERTHIER, *Ann. Ch. et Ph.*, L. 370, and N.S. vii. 77.)

HYPOSULPHATE OF CHROMIUM. $\text{Cr}_2\text{O}_3, \text{S}_2\text{O}_5$, forms small violet octohedra, soluble in water. (BERTIN.)

SULPHATE OF CHROMIUM. When hydrated oxide of chromium is dissolved in dilute sulphuric acid a green solution is obtained, and on evaporation an insoluble *subsalt* remains. When pulverised bichromate of potassa is gradually added to hot concentrated sulphuric acid, oxygen is liberated, and an insoluble violet powder deposited, which may be perfectly separated by dilution with water; the acid liquid contains bisulphate of potassa, but no trace of chromium. This sulphate when dried forms a green powder, which becomes rose-colored and very mobile on exposure to heat: it is then insoluble in water. Its formula is $\text{Cr}_2\text{O}_3, + 3\text{SO}_3$. Subjected at a dull red-heat to a current of dry hydrogen its oxygen is carried off together with part of the sulphur, and a brown and highly pyrophoric sulphuret of chromium remains $= \text{Cr}_4\text{S}_3$. By combustion in air or oxygen it becomes Cr_4O_6 ; it therefore retains exactly or nearly the same weight before and after combustion, the 3 atoms of sulphur $= (16 \times 3 = 48)$ being replaced by 6 of oxygen $= (8 \times 6 = 48.)$ (E. KOPP. *Comptes Rendus*, June, 1844.)

When a solution of 8 parts of hydrate of sesquioxide of chromium in 9 of cold sulphuric acid is left to itself in a covered basin, it concretes in a few weeks into a blue-green crystalline mass: when this is dissolved in water and alcohol added, a pale blue crystalline powder falls, which may be obtained in octohedral crystals soluble in less than their weight of water at 68° , and which at 212° lose water and become green. Their formula is $\text{Cr}_2\text{O}_3, 3\text{SO}_3, 15\text{HO}$. (SCHRÖTTER. *Poggend.*, liii. 513.)

AMMONIO-SULPHATE OF CHROMIUM. $\text{NH}_4\text{O}, \text{SO}_3 + \text{Cr}_2\text{O}_3, 3\text{SO}_3, + 24\text{HO}$. This salt forms purple octohedral crystals. (HAIDINGER, *Edin. Jour. of Science*, i. 100.) It is the *ammoniacal chrome-alum* of Mitscherlich, composed of

					Schrötter.	
Ammonia	1	17	3·53	
Sesquioxide of chromium.....	1	80	16·59 16·26
Sulphuric acid	4	160	33·20 33·10
Water	25	225	46·68	
<hr/>						
Crystals of ammoniacal chrome-alum	1		482		100·00	

The solution of this salt in cold water is blue, but it becomes green when heated to about 175° , and is then decomposed and no longer affords crystals on evaporation; but if the green solution be diluted with water till it becomes blue it then again affords the alum on standing for 10 days, or on the addition of alcohol.

POTASSA-SULPHATE OF CHROMIUM. CHROME-ALUM. $\text{KO}, \text{SO}_3, + \text{Cr}_2 \text{O}_3, 3\text{SO}_3 + 24\text{HO}$. When a mixed solution of acid sulphate of chromium and sulphate of potassa is left to spontaneous evaporation, regular octohedral crystals, appearing purple in one direction, and green in another, are deposited. (BERZELIUS.) 2. To a solution of bichromate of potassa add successively sulphuric acid and alcohol till it becomes deep green; it then yields the crystals, on spontaneous evaporation. (FISCHER.) 3. Pass sulphurous acid through an aqueous solution of 1 atom of bichromate of potassa and 1 of oil of vitriol, avoiding elevation of temperature.

When this salt is dissolved in water, and the solution evaporated, it can only be again obtained in regular crystals when excess of sulphuric acid is present, by which the solubility of the salt is diminished. This salt has been called *chrome-alum*, inasmuch as if aluminum were substituted for chromium, common alum would be the result; so that there are not less than four isomorphous oxides which give aluminoid salts with potassa and sulphuric acid, namely, those of aluminum, manganese, iron, and chromium. The components of this salt are

						Berzelius.
Potassa	1	48	9.52 9.38
Sesquioxide of chromium.....	1	80	15.87 15.90
Sulphuric acid	4	160	31.75 31.80
Water	24	216	42.86 42.92
<hr/>						<hr/>
Crystals of chrome-alum	1		504		100.00	100.00

CHROMOSULPHATE OF POTASSA. When solutions of chromate and of sulphate of potassa are mixed and evaporated, a double salt is obtained, containing 43.3 of chromate and 56.7 of sulphate of potassa; it forms pale yellow prismatic crystals, and yields a precipitate with nitrate of baryta, which is only partially soluble in nitric acid. It has occasionally been substituted for chromate of potassa. It has a bitterish taste, and is readily soluble in cold and hot water. (BOUTRON-CHARLARD. *Jour. de Pharm.*, ix. 184.)

PHOSPHURET OF CHROMIUM. Cr_2P . When phosphate of chromium is intensely heated with charcoal a grey phosphuret is obtained. When phosphuretted hydrogen gas is passed over sesquichloride of chromium at a red-heat, a black phosphuret is the result, which burns before the blow-pipe, and is insoluble in hydrochloric acid. (ROSE, *Poggend.*, xxiv. 333.)

HYPOPHOSPHITE OF CHROMIUM, is formed by the double decomposition of sulphate of chromium and hypophosphite of baryta: on evaporation an amorphous dark-green mass remains, which heated to 392° becomes insoluble in water and in dilute acids. The formula of the hydrated salt is $\text{Cr}_2 \text{O}_3, 2\text{PO}, 6\text{HO}$. (WURTZ.)

PHOSPHITE OF CHROMIUM, falls in the form of a green powder when ammonioterchloride of phosphorus is added to an aqueous solution of sesquichloride of chromium: when heated it evolves hydrogen. (H. ROSE, *Poggend.*, ix. 40.)

PHOSPHATE OF CHROMIUM. When phosphate of potassa is added to a solution of sesquichloride of chromium a green precipitate falls. The solution of hydrated oxide of chromium in phosphoric acid is emerald green and uncrystallizable. (VAUQUELIN.)

CARBONATE OF CHROMIUM. The blue-green precipitate which the carbonated alkalis produce in solutions of the sesquisalts of chromium, is not a true carbonate, but a compound of subcarbonate and hydrate of oxide of chromium. (BERZELIUS.) It dissolves, according to Meissner, (who regards it as a true carbonate,) in solution of carbonate of potassa, forming a grass-green liquid, and is sparingly soluble in carbonate of ammonia: it loses its carbonic acid at 142° .

BORATE OF CHROMIUM. Borate of ammonia produces a green insoluble precipitate in solution of chloride of chromium. Borax gives a blue precipitate soluble in excess of the boracic solution.

ARSENATE OF CHROMIUM. When mixed solutions of arseniate of soda and sesquichloride of chromium are evaporated to dryness, and the residue digested in water, an insoluble green powder remains, composed of arsenic acid and sesquioxide of chromium. When hydrated sesquioxide of chromium is digested in an aqueous solution of arsenic acid, a dark-green liquid is formed which leaves a green insoluble residue on evaporation: when heated red-hot it becomes rose-red, but buff-colored on cooling: it is a *binarsenate of chromium*. (THOMSON.) Arseniate of potassa gives an apple-green precipitate with solutions of oxide of chromium. (MOSER.)

MOLYBDATE OF CHROMIUM. A green precipitate falls when solutions of sesquichloride of chromium and molybdate of potassa or of ammonia are mixed, which is soluble in excess of the molybdate of ammonia. (BERZELIUS.)

ALLOYS OF CHROMIUM. Nothing is known of the alloys of chromium with the light metals: nor with manganese. With *iron*, it apparently unites in all proportions: this alloy is obtained by strongly heating mixtures of the oxides of chromium and of iron in a covered charcoal crucible. An alloy of 4 atoms of chromium with 1 of iron is crystalline, whiter than platinum, and very hard and brittle. Steel containing from 1 to 2 *per cent.* of chromium answers well for cutting instruments. (BERTHIER, *Ann. des Mines*, vi. 579. *Ann. Ch. et Ph.*, xvii. 55. FARADAY, *Phil. Trans.*, cxii. 253.) The other alloys of chromium have not been examined.

GENERAL CHARACTERS OF THE SALTS OF CHROMIUM. The peculiar characters of the combinations of chromium, of the salts of the sesquioxide, and of the chromic acid, will be sufficiently evident from their preceding enumeration. Before the blow-pipe, oxide of chromium exhibits the following properties: it is fusible with microcosmic salt in the interior flame into a glass, which at the instant of its removal from the flame is of a violet hue, approaching more or less to dark blue or red, according to the proportion of the chromium. After cooling, the glass is bluish-green, but less blue

than copper glass. In the exterior flame the color becomes brighter, and less blue than the former. With borax it forms a bright-yellowish or yellow-red glass in the exterior flame; and in the interior flame this becomes darker and greener, or bluish-green.

§ XXVII. VANADIUM. V. 68.

THIS metal was discovered by Seftström in the year 1830; its name is derived from *Vanadis*, a Scandinavian deity; he found it in the ores of iron from Taberg in Sweden, and in the slags from the reducing furnaces. The same metal was shortly after found by Johnston, in a lead ore from Wanlock-head, and by Del Rio in a lead ore from Zemapan in Mexico: the latter terms it *Erythronium*, from the red color of its acid. Thus have three persons noticed the existence of vanadium without the knowledge of each other's labors, but the merit of being its discoverer is due to Seftström. (*Phil. Mag. and Ann.*, x. 321; *Ann. Ch. et Ph.*, XLvii. 377; *Poggend. Ann.*, xxii. 1.)

Vanadium is most readily obtained from the native *vanadate of lead*, by the following process of Johnston. (*Edin. Journ. of Science*, v. 166 and 318.) The ore is dissolved in nitric acid, and a current of sulphuretted hydrogen passed through the solution, by which lead and arsenic are precipitated, and a blue solution is obtained, which is evaporated to dryness; the residue is dissolved in ammonia, and a piece of sal-ammoniac larger than it can dissolve is introduced into the solution; *vanadate of ammonia* then subsides in the form of a white powder, which should be washed, first with a solution of sal-ammoniac (in which it is insoluble), and then with alcohol of the specific gravity 0.86. This salt may be decomposed by heating and stirring it in a platinum crucible till it acquires a red color; it is then *vanadic acid*. When this is intensely heated in a charcoal crucible it is superficially reduced. Berzelius succeeded in reducing this acid by the action of potassium, which at a moderate heat suddenly decomposes it, and on washing the residue, vanadium remains in a pulverulent form. Vanadium may also be obtained by decomposing chloride of vanadium by a current of dry ammonia, and heating the white saline mass which is so produced: the terchloride is introduced into a bulb blown in a glass tube and heated over an argand spirit-lamp; sal-ammoniac sublimes, and metallic vanadium remains.

Vanadium, as resulting from the decomposition of the chloride, has somewhat of a silvery lustre, is extremely brittle, conducts electricity, and is not acted upon by air or water at common temperatures; at a dull red-heat it takes fire and burns into a black oxide; it is not acted upon by sulphuric, hydrochloric, or hydrofluoric acids, but nitric and nitrohydrochloric acids yield dark-blue solutions; it is not acted on by boiling caustic potassa, nor by the alkaline carbonates at a red-heat: its equivalent is 68. (68.5 TURNER. 68.66 GRAHAM. 68.6 GMELIN.)

VANADIUM AND OXYGEN. There are three compounds of this metal with oxygen; two oxides, and an acid.

PROTOXIDE OF VANADIUM. VO. When a stream of dry hydrogen

gas is passed over heated vanadic acid, water is formed, in consequence of the partial reduction of the acid, and a black substance remains, which is extremely infusible, conducts electricity, is strongly electro-negative in relation to zinc, and which, when heated in the air, is converted by slow combustion into the binoxide. It is not salifiable. From these characters, this substance, if not vanadium, would appear to be a mixture of the metal with a portion of the oxide: according to Berzelius it is a *protoxide*. Exposed to air and moisture it slowly absorbs oxygen, and when kept in water gradually communicates to it a green tint: the same change occurs in alkaline and acid solutions, and with the exception of nitric and nitrohydrochloric acids, it is not dissolved by them. It consists of

						Berzelius.
Vanadium	1	...	68	...	89.5	89.538
Oxygen	1	...	8	...	10.5	10.462
<hr/>						<hr/>
Protoxide of vanadium.....	1		76		100.0	100.000

BINOXIDE OF VANADIUM. VANADIOUS ACID. VO_2 . When 10 parts of protoxide and 12 of vanadic acid are intimately mixed and heated in an exhausted vessel, or in one filled with carbonic acid, a black compound is obtained, which is the binoxide. This is the only salifiable oxide: it may be obtained in the state of *hydrate*, by precipitation from its acid solutions by carbonate of soda in very slight excess; if carefully dried out of the contact of air is of a grey color, and gives out its water when heated. In this hydrated state it yields blue solutions with the acids: it also dissolves in caustic potassa and in ammonia, forming brown liquids. It is composed of

						Berzelius.
Vanadium	1	...	68	...	80.9	81.056
Oxygen	2	...	16	...	19.1	18.944
<hr/>						<hr/>
Binoxide of vanadium	1		84		100.0	100.000

VANADIC ACID. VO_3 . When vanadate of ammonia is moderately heated and stirred in an open vessel, it gradually acquires a red color, and leaves vanadic acid: heated in a close vessel, the hydrogen of the ammonia deoxidizes the acid, and the binoxide is the product; vanadic acid, when fused, is red, but when in powder, brown: it fuses at a dull red-heat, and in the act of crystallizing, as it cools, it contracts in bulk, and gives out so much latent heat as to become incandescent. It undergoes no change by heat, provided all deoxidizing agents are excluded; when any combustible matter is present, it passes into the state of oxide: it is tasteless, insoluble in alcohol, and nearly so in water. Vanadic acid consists of

						Berzelius.
Vanadium	1	...	68	...	73.9	74.045
Oxygen	3	...	24	...	26.1	25.955
<hr/>						<hr/>
Vanadic acid	1		92		100.0	100.000

VANADIATES. The compounds of vanadic acid with salifiable bases are generally orange-colored or yellow, but they sometimes are produced colorless, without any apparent change of composition: it forms neutral

and bi-salts, those with the alkalis being soluble, and with the other oxides, either sparingly soluble or insoluble. The soluble salts are easily deoxidized by alcohol, sulphuretted hydrogen, sulphurous acid, and several of the hydracids. Vanadic acid dissolves and forms variously colored compounds with the binoxide of vanadium: these compounds are formed when the binoxide in water is exposed to air; it gradually forms vanadic acid, and the solution becomes blue, green, yellow, and red, according to the extent of acidification. It also combines with some of the other acids, as is the case with the chromic acid.

The color of vanadic acid distinguishes it from others, with the exception of the chromic, with which it was at first confounded; but the *blue* color, as opposed to the green produced by deoxidizing substances with chromic acid, is a distinctive character. When heated with borax before the blow-pipe it produces, like chromic acid, a green bead in the reducing flame; but in the exterior flame, the green remains if from chromium, but becomes yellow if from vanadium.

SALTS OF THE BINOXIDE OF VANADIUM. The salts of the binoxide of this metal are best obtained by the action of the respective acids upon the hydrated binoxide: they are blue, and afford a grey precipitate with the alkalis, which when exposed to air becomes red: infusion of galls blackens them. The *nitrate of vanadium*, which is at first blue, becomes red during evaporation, from the formation of vanadic acid.

CHLORIDES OF VANADIUM. When binoxide of vanadium is digested in hydrochloric acid, a brown solution is obtained, which appears to contain a *bichloride*, VCl_2 . When vanadic acid is digested in hydrochloric acid, chlorine is evolved, and a blue solution is formed, which by evaporation becomes brown, but from which a dry chloride cannot be obtained. When dry chlorine is passed over a red-heated mixture of protoxide of vanadium and charcoal, in a glass or porcelain tube, a yellow liquid is obtained, which when acted upon by water yields hydrochloric and vanadic acids; it is therefore a *terchloride*, VCl_3 . By the action of hydriodic, hydrobromic, hydrofluoric, and hydrocyanic acids upon the oxide, an *iodide*, *bromide*, *fluoride*, and *cyanide* of vanadium may be obtained.

SULPHURETS OF VANADIUM. By passing a current of sulphuretted hydrogen over the binoxide heated to redness, a *bisulphuret of vanadium* is ultimately obtained. The same compound is formed when hydrosulphuret of ammonia is mixed with a solution of a salt of vanadium, till the precipitate first formed is redissolved, and then, decomposing the deep purple solution by sulphuric or hydrochloric acid: a brown bisulphuret subsides, which becomes black when it is dried. In the hydrated state it is dissolved by the alkalis and alkaline sulphurets, but is insoluble in the acids, with the exception of the nitric and nitrohydrochloric, by which it is converted into sulphate. When sulphuretted hydrogen is passed through vanadic acid in water, a mixture of hydrated binoxide and sulphur is precipitated; but when a solution of vanadic acid in hydrosulphuret of ammonia is acidulated by hydrochloric or sulphuric acid, a hydrated *ter-sulphuret* subsides; its color is at first light brown, but it becomes almost

black by drying, and when heated to redness in close vessels, it gives off water and sulphur, and is resolved into the bisulphuret. It dissolves in alkalis and in alkaline sulphurets.

PHOSPHURET OF VANADIUM. When phosphate of vanadium mixed with a little sugar is exposed to a white heat, a grey phosphuret is obtained.

The history of the salts and other compounds of vanadium is given in detail by Gmelin in his *Handbuch*, and by Berzelius in his *Lehrbuch der Chemie*.

§ XXVIII. TUNGSTEN. W. 100.

THIS metal, which has also been called *Scheelium* and *Wolframium*, was first obtained by Messrs. de Luyart, from the *tungstic acid* previously discovered by Scheele, in 1781. Its native sources are *wolfram*, which is a *tungstate of iron and manganese* (EBELMEN, *Ann. Ch. et Ph.*, Août, 1843), and the *tungstate of lime*. It is obtained by exposing a mixture of tungstic acid and charcoal to an intense heat; or by passing hydrogen over the ignited acid. It is very difficult of fusion, very hard, brittle, and of an iron color. Its specific gravity 17·4. Its approximate specific heat is 0·03636. (REGNAULT.) It is oxidized by the action of heat and air, and by nitric acid. It is also oxidized and gradually dissolved by solution of potassa, with the evolution of hydrogen, and *tungstate of potassa* is produced. A piece of zinc immersed in a solution of tungstate of ammonia throws down metallic tungsten in the form of a brown powder. (DUMAS.) The equivalent of tungsten may be assumed at about 100. (94·8 GRAHAM: 96 GMELIN: 99·7 TURNER.)

OXIDE OF TUNGSTEN. BINOXIDE OF TUNGSTEN. WO_2 . This oxide may be obtained by mixing finely-powdered wolfram with twice its weight of carbonate of potassa, and fusing it in a platinum crucible. Tungstate of potassa is thus formed, which is dissolved in hot water with half its weight of sal-ammoniac, evaporated to dryness, and heated red-hot in a Hessian crucible. The mass is then well washed in boiling water, and digested in weak solution of potassa. The residue is oxide of tungsten. In this process the tungstate of potassa and sal-ammoniac form chloride of potassium and tungstate of ammonia; but at a red-heat the ammonia decomposes the tungstic acid, and reduces it to the state of oxide, which is prevented by the fused chloride of potassium from passing into the state of acid. (WÖHLER, *Quart. Journ.*, xx. 177.) Thus prepared, the oxide is black, and when heated to redness, it suddenly ignites and becomes converted into tungstic acid by the absorption of oxygen. Its sp. gr. is 12·1. It does not appear capable of entering into combination with the acids so as to form salts. When a current of hydrogen gas is carefully passed over heated tungstic acid, it is partially deoxidized and converted into a chocolate-colored oxide, which neither combines with acids nor with bases, and which is identical in composition with the above. (*Ann. Ch. et Ph.*, xvii. 16.) If the action of hydrogen be too long continued, the oxide itself is reduced. This oxide consists of

							Berzelius.
Tungsten	1	...	100	...	86.21	...	85.54
Oxygen	2	...	16	...	13.79	...	14.46
<hr/>							<hr/>
Oxide of tungsten	1		116		100.00		100.00

Wöhler has described an interesting combination of this oxide with soda, which is obtained by adding as much tungstic acid to fused tungstate of soda as it will dissolve, and then passing hydrogen over the compound at a red-heat: on washing out the undecomposed tungstate with water, a golden-colored substance remains, in small cubes and scales of a beautiful metallic lustre, and insoluble in caustic alkalis and in nitric, sulphuric, and nitrohydrochloric acids, but soluble in hydrofluoric acid. At a red-heat, oxygen, chlorine, and sulphur decompose it. It cannot be obtained by the direct combination of soda with the oxide. (*Poggend.*, ii. 345.) It consists of

							Wöhler.
Soda	1	...	32	...	12	...	12.4
Oxide of tungsten	2	...	232	...	88	...	87.6
<hr/>							<hr/>
	1		264		100		100.0

TUNGSTIC ACID, WO_3 , is obtained when the oxide is heated red-hot, and stirred in an open vessel. When finely-powdered native tungstate of lime is boiled for some hours in nitric acid, tungstic acid is separated, in the form of a yellow powder, which may be freed from adhering nitric acid, by dissolving it in ammonia, and heating the tungstate of ammonia to redness. Tungstate of potassa, prepared by heating wolfram with carbonate of potassa, as above described, may also be decomposed by nitric acid, and the precipitate treated with ammonia as before. Tungstate of lime may also be decomposed by digestion in hydrochloric acid; chloride of calcium and tungstic acid are the results. In all cases where tungstic acid has been in contact with an acid, or where it is precipitated from its alkaline solutions by acids, the precipitate which falls retains traces of the foreign acid: hence the advantage of forming a tungstate of ammonia and decomposing it by heat only.

Tungstic acid is a yellowish powder, which appears green whilst hot, and also acquires a greenish color by long exposure to the sun's rays. Its specific gravity is about 6. It is insoluble in water, but readily soluble in the caustic alkalis, when in its hydrated state; after it has been heated it is very difficultly acted upon by solvents, but most of its compounds may be obtained by fusion at a red-heat. When precipitated by the acids from its ammoniacal solution, a portion of the precipitant is carried down with it, and in this way compounds of sulphuric, nitric, and hydrochloric acids, with tungstic acid, may be produced, which are more or less soluble in water.

When tungstic acid is exposed to a heat of about 600° in a current of hydrogen, it becomes blue; a similar product is obtained when metallic zinc is put into a mixture of hydrochloric and tungstic acids; or when tungstate of ammonia is decomposed by distillation in a retort. This has sometimes been regarded as a distinct oxide, W_2O_3 , (*MALAGUTI, Ann. Ch. et Ph.*, LX. 271;) but, according to Berzelius, it is a tungstate

of the oxide, or a compound of the acid and oxide. Tungstic acid consists of

						De Luyart.	Bucholz.	Berzelius.			
Tungsten	1	...	100	...	80·6	...	80·64	...	80	...	79·766
Oxygen	3	...	24	...	19·4	...	19·36	...	20	...	20·234
<hr/>											
Tungstic acid	1		124		100·0		100·00		100		100·000

GENERAL PROPERTIES OF THE TUNGSTATES. The alkaline and earthy tungstates are colorless: they are heavy; and those which are soluble have a bitter metallic taste; hydrochloric, nitric, and sulphuric acids occasion in them white precipitates; phosphoric acid forms with them soluble triple compounds. When their acid solutions are acted upon by zinc, they acquire the blue color above adverted to. The tungstates which are not decomposed by heat are fusible.

TUNGSTATE OF AMMONIA is procured in crystalline scales, sparingly soluble in water, and of a metallic taste, by digesting the acid in ammonia. It contains, according to Berzelius,

						Berzelius.	
Ammonia.....	1	...	17	...	6.0	...	6.338
Tungstic acid	2	...	248	...	87.6	...	87.000
Water	2	...	18	...	6.4	...	6.662
<hr/>							
Tungstate of ammonia....	1		283		100.0		100.000

TUNGSTATE OF POTASSA is uncrystallizable (or very difficultly crystallizable) and deliquescent; it has a styptic and acrid taste. The acids occasion precipitates in its solution, which are triple compounds of tungstic acid, potassa, and the acid used as a precipitant. The *Nitrotungstate of Potassa* is the salt originally described by Scheele as tungstic acid. It dissolves in 20 parts of water at 212°, and reddens litmus. Tungstate of potassa, when neutral, is not affected at high temperatures by hydrogen, but the acid tungstate has its excess of acid decomposed and reduced. The neutral salt when crystallized is $\text{KO}, \text{WO}_3, 5\text{HO}$, and the bitungstate = $\text{KO}, 2\text{WO}_3, 2\text{HO}$. (ANTHON. *Journ. Prakt. Chem.*, viii. and ix.)

TUNGSTATE OF SODA crystallizes in hexahedral tables, soluble in 4 parts of cold, and in 2 of boiling water, and of an acrid taste. Sulphuric, nitric, and hydrochloric acids occasion precipitates, as in the tungstate of potassa. *Bitungstate of Soda* is easily crystallizable and soluble in 8 parts of water at 60°. By hydrogen at a red-heat it is reduced to neutral tungstate, and a compound of soda and oxide of tungsten, as above stated. The crystallized neutral tungstate includes 2 atoms, and the bitungstate 4 atoms of water. (ANTHON.)

TUNGSTATE OF LIME, OF BARYTA, AND OF STRONTIA, are insoluble white compounds. *Native Tungstate of Lime* is the substance from which Scheele originally obtained tungstic acid; it generally accompanies tin ore in Bohemia, Saxony, and Cornwall: fine specimens have also been found in Cumberland: it is white or nearly so; its primary form

is an octohedron with a square base; its density about 6. It is constituted of

							<i>Native.</i>
							<i>Berzelius.</i>
Tungstic acid	1	...	124	...	81.6	...	80.417
Lime	1	...	28	...	18.4	...	19.400
<hr/>							<hr/>
Tungstate of lime	1		152		100.0		99.817

TUNGSTATE OF MAGNESIA is obtained by boiling the acid with magnesia, filtering, and evaporating; it crystallizes in pearly scales. The acids produce precipitates of triple compounds in its solution.

TUNGSTATE OF MANGANESE, formed by adding tungstate of potassa to hydrochlorate of manganese, is an insoluble white powder. (JOHN, *Gehlen's Journal*, iv.) *Tungstate of Iron* is also insoluble. *Tungstate of Zinc and of Tin* have not been described, nor have any of the remaining tungstates been examined in their pure state.

Native Tungstate of Iron and Manganese, or *Wolfram*, commonly accompanies tin stone, and is found in Cornwall and in many of the tin mines of Saxony and Bohemia: it has also been found in Siberia, and in the United States of America; its color is nearly black, and it occurs massive and crystallized, its primary form being a right oblique-angled prism: its specific gravity is 7.15. A specimen analyzed by Richardson, gave 73.60 tungstic acid, 11.20 protoxide of iron, 15.75 protoxide of manganese: these numbers are nearly the equivalents of 3 atoms of tungstate of iron, and 4 atoms of tungstate of manganese. (THOMSON, *Mineralogy*, i. 487. See also in reference to the composition of different varieties of wolfram, SCHAFFGOTSCH, *Ann. Ch. et Ph.*, 3 Ser. ii. 532.)

CHLORIDE OF TUNGSTEN. WCl_2 . When metallic tungsten is heated in chlorine, it burns and forms a red crystalline compound, which is fusible and volatile, and which, according to Wöhler, becomes blue in water, forming hydrochloric acid, and depositing a suboxide. It is soluble in caustic potassa with the evolution of hydrogen, and yields tungstate of potassa and chloride of potassium. It consists of

							Malaguti.
Tungsten	1	...	100	...	58	...	57.6
Chlorine	2	...	72	...	42	...	42.4
<hr/>							<hr/>
Chloride of tungsten	1		172		100		100.0

PERCHLORIDE OF TUNGSTEN. WCl_3 . When sulphuret of tungsten is heated in a current of chlorine, it burns, and forms a *perchloride*, which condenses in red acicular crystals. This chloride is resolved by the moisture of the air into tungstic and hydrochloric acids; when gently heated, it rises in the form of a dark-yellow vapor before it fuses: heated on a slip of platinum in the flame of a spirit-lamp, it is decomposed by the water of the flame, and yields hydrochloric and tungstic acid; the latter forms a luminous fume, and condenses in large light flocks. It consists of

							Malaguti.
Tungsten.....	1	...	100	...	48.1	...	47.4
Chlorine	3	...	108	...	51.9	...	54.6
<hr/>							<hr/>
Perchloride of tungsten	1		208		100.0		100.0

According to H. Rose (*Ann. Ch. et Ph.*, LXvi. 215), the compound obtained by heating oxide of tungsten in chlorine, is an *oxichloride of tungsten*, or a tungstate of chloride of tungsten, composed of $2\text{WO}_3, \text{WCl}_3$, or of

						H. Rose.
Tungsten	3	300	65·8 64·80
Oxygen	6	48	10·5 10·95
Chlorine	3	108	23·7 24·25
<hr/>						
Oxichloride of tungsten	1		456		100·0	100·00

BROMIDE OF TUNGSTEN appears to be formed by passing bromine vapor over a red-hot mixture of tungstic acid and charcoal: with excess of bromine, and at a higher temperature, the compound obtained is an *oxibromide* $= \text{WO}_3 + 2\text{WBr}_3$. (BONNET. *Journ. Prakt. Chem.*, x. 206.)

SULPHURETS OF TUNGSTEN. When 1 part of tungstic acid is mixed with 6 of cinnabar, and heated intensely for half an hour; or when the vapor of sulphur, or sulphuretted hydrogen, is passed over tungstic acid heated intensely in a porcelain tube, a black powder is obtained, which assumes metallic lustre by friction, and which consists, according to Berzelius, of 100 tungsten + 33·6 sulphur: it is therefore a *bisulphuret* $= \text{WS}_2$.

When tungstic acid is dissolved in hydrosulphuret of potassa, and precipitated by dilute sulphuric acid, a compound falls of a dirty-yellow color, and somewhat soluble in water, which, according to Berzelius, is a *tersulphuret* $= \text{WS}_3$, the mode of its formation being as follows: $2\text{WO}_3 + 3[\text{KO}, \text{HS}] + 3\text{SO}_3 = 2\text{WS}_3 + 6\text{HO} + 3[\text{KO}, \text{SO}_3]$; it becomes darker colored when dried, and when heated in close vessels, first gives off a little water, and then its excess of sulphur: it leaves the bisulphuret.

PHOSPHURET OF TUNGSTEN. Pelletier formed this compound, but its properties have not been examined. (*Ann. de Chim.*, xiii. 137.)

CHARACTERS OF THE COMPOUNDS OF TUNGSTEN. The general properties and tests of tungsten and its compounds will be evident from the preceding details. Before the blow-pipe, tungstic acid becomes upon charcoal at first brownish-yellow, is then reduced to a brown oxide, and lastly, becomes black without melting or smoking. With microcosmic salt it forms in the interior flame a pure blue glass, without any violet tinge; in the exterior flame this color disappears, and appears again in the interior. With borax, in the internal flame, and in small proportion, it forms a colorless glass, which, by increasing the proportion of acid, becomes dirty-grey, and then reddish. By long exposure to the external flame it is rendered transparent, but as it cools it becomes muddy, whitish, and changeable into red when seen by daylight. It is not reduced. When *wolfram* is heated before the blow-pipe, it first decrepitates, and, at a high temperature, fuses into a crystalline globule of metallic lustre; with borax it forms a green bead, and with biphosphate of soda it fuses into a deep red globule. Tungstate of lime, when heated by the blowpipe-flame, crackles and becomes opaque, but does not fuse; with borax, it fuses into a globule.

§ XXIX. COLUMBIUM. Ta. 185.

THIS metal was discovered in 1801 by Mr. Hatchett, in a mineral from North America. (*Phil. Trans.*, 1842, p. 49.) It was afterwards found by Ekeberg combined with the oxides of iron and manganese, and also with yttria, in the Swedish minerals called *tantalite* and *yttro-tantalite*. (*Crell's Ann.*, 1803.) Tantalite is chiefly found in octohedral crystals, and in masses of a black or grey color, in Finland. Its specific gravity is 7·9, and it contains, according to Ekeberg, 80 oxide of columbium, 12 oxide of iron, and 8 oxide of manganese. Yttro-tantalite is found at Ytterby, in Sweden, in a rock of red felspar and mica; it is usually in small masses, plates, or grains; there are three varieties which have been analyzed by Berzelius, with the following results:

	Black.		Yellow.		Brown.
Columbic acid	57·00	60·124	51·815
Yttria	20·25	29·730	38·515
Lime	6·25	0·500	3·260
Tungstic acid	8·25	1·044	2·592
Peroxide of iron.....	3·50	1·155	0·555
Oxide of uranium	0·50	6·622	1·111
	<hr/>		<hr/>		<hr/>
	95·75		99·225		97·848

There is also a mineral found near Cape Farewell, in East Greenland, and which has been called *Fergusonite*; it occurs crystallized in octohedra and their modifications; its density is 5·7 to 5·8; its color brownish-black; it was first described by Haidinger (*Edin. Phil. Trans.*, x. 274), and was analyzed by Hartwell; its constituents are

Columbic acid	47·75
Yttria	41·91
Protoxide of cerium	4·68
Zirconia	3·02
Oxide of tin.....	1·00
Oxide of uranium	0·95
Peroxide of iron	0·34
	<hr/>
	99·65

When columbium was discovered in the Swedish minerals by Ekeberg, he considered it as a *new* metal, and called it *tantalum*. In 1809 (*Phil. Trans.*) Wollaston re-examined these, and the specimen in the British Museum, originally analyzed by Hatchett, and demonstrated the identity of columbium and tantalum. As the former name was given to this metal by its original discoverer, it is here retained; by foreign writers it is usually called *tantalum*, and represented by the symbol Ta.

Columbite and tantalite may be decomposed by the following process: Mix 5 parts of the finely-powdered mineral with 25 of carbonate of potassa, and 10 of borax; fuse the mixture, and, when cold, digest it in hydrochloric acid; this dissolves everything except the peroxide of columbium, which remains in the form of a white powder. (WOLLASTON, *Phil. Trans.*, 1809, p. 248.) From 5 grains of *columbite*, Dr. Wollaston obtained 4 grains of oxide of columbium, 0·75 of oxide of iron, and 0·25 of oxide of manganese; and from 5 grains of *tantalite* he procured 4·25 of oxide of columbium, 0·50 of oxide of iron, and 0·2 of oxide of manganese.

Berzelius obtained metallic columbium by heating potassium with the *potassio-fluoride of columbium*, and washing the reduced mass with water. It remains in the form of a black powder; by pressure it acquires the lustre and color of iron; it burns at a red-heat into a whitish oxide. Its specific gravity is about 6. It is insoluble, or nearly so, in hydrochloric, nitric, and nitrohydrochloric acids; but is acted on by hydrofluoric acid. Heated to redness, it burns into columbic acid. Mixed with nitre, and projected into a red-hot crucible, it detonates, and is oxidized. It forms alloys with other metals. (*Ann. Ch. et Ph.*, iii. 140.) Its equivalent may be assumed as 185. (185 GMELIN, 184·9 GRAHAM.)

OXIDE OF COLUMBIUM. TANTALOUS ACID. TaO_2 . When columbic acid is intensely heated for an hour and a half in a charcoal crucible, it is superficially reduced to a metallic state, but the interior portion is a dark-grey oxide, becoming brown when pulverized; it is insoluble in the acids, but may be peroxidized by fusion with potassa: it burns when heated in the air: it consists of

						Berzelius.
Columbium	1	185	92·04 92·02
Oxygen	2	16	7·96 7·98
<hr/>						<hr/>
Oxide of columbium	1		201		100·00	100·00

COLUMBIC ACID. TANTALIC ACID. TaO_3 . The best process for obtaining columbic acid consists in fusing the ore of columbium with bisulphate of potassa, and proceeding as directed by Berzelius. (*Lehrbuch.*) An easier, but less economical process, is that of Ekeberg, in which the ore is finely powdered, and fused with caustic potassa; a soluble columbate of potassa is formed, from which the columbic acid may be precipitated, as a white *hydrate*, by the acids. Dr. Wollaston's process, above given, may also be used. The characters of columbic acid are very well marked. In its anhydrous state, after having been ignited, its sp. gr. is 6·5: it is nearly insoluble in hydrochloric, nitric, and sulphuric acids; it is soluble in potassa, and carbonate of potassa: 8 grains of the latter, fused with 1 of the oxide, render it soluble in water. It is much less soluble in soda, and only retained while hot.

The hydrated columbic acid ($TaO_3, 3HO$) dissolves in nitric, hydrochloric, and sulphuric acids, and, according to Wollaston, in tartaric, citric, and oxalic acids. In this state, and whilst moist, it is abundantly soluble in solution of binoxalate of potassa, but scarcely at all in bitartrate of potassa. The oxalic solution is colorless; alkalis throw down the columbic acid; ferrocyanide of potassium produces in it a yellow precipitate; infusion of galls gives it an orange color, and when added in excess, produces a precipitate; the hydrosulphurets occasion a white precipitate, with the evolution of sulphuretted hydrogen. Columbic acid consists of

						Berzelius.
Columbium	1	185	88·5 88·49
Oxygen	3	24	11·5 11·51
<hr/>						<hr/>
Columbic acid	1		209		100·0	100·00

COLUMBATE OF AMMONIA is produced by digesting hydrated columbic acid in ammonia: it is insoluble, and at a red-heat yields ammonia and

water: the ammonia escapes by long exposure to air. Carbonate of ammonia only takes up a trace of columbic acid.

COLUMBATE OF POTASSA is obtained by fusing columbic acid with carbonate of potassa, pulverizing the product, and digesting it in water. The columbate of potassa, being nearly insoluble in a solution of carbonate of potassa, remains, and after it has been washed with a little cold water, it may be dissolved in boiling water; when this solution is distilled to dryness, a saline uncrystallizable mass remains, of an unpleasant metallic taste; its solution is precipitated by all the acids, not excepting the carbonic.

COLUMBATE OF SODA may be obtained as the preceding: it is less soluble, and is almost entirely deposited, as a white powder, during the cooling of its boiling aqueous solution.

COLUMBATE OF LIME and OF BARYTA are insoluble white powders.

FERRO-COLUMBATE OF MANGANESE has been adverted to above as a natural product, under the name of *columbite*, or *tantalite*.

The remaining binary salts of the columbic acid with the oxides have not been examined.

CHLORIDE OF COLUMBIUM. The metal burns when heated in chlorine, producing a yellow vapor, which condenses into a white pulverulent substance, which, on contact of water, is converted, with rapid action and increase of temperature, into hydrochloric and columbic acids: this is therefore a *terchloride*.

FLUORIDE OF COLUMBIUM. When hydrated columbic acid is dissolved in hydrofluoric acid, and evaporated at a temperature of about 86° , crystals are obtained, which dissolve without residue in water, and which consist of fluoride of columbium and hydrofluoric acid. (BERZELIUS.) This compound combines with other fluorides to form *columbo-fluorides*.

SULPHURET OF COLUMBIUM. When columbium is heated in the vapor of sulphur it burns into a sulphuret: a similar compound is formed by passing the vapor of sulphuret of carbon over columbic acid heated to whiteness in a porcelain tube. In the air this sulphuret burns into columbic acid, which obstinately retains a portion of sulphuric acid. Berzelius considers this as a *tersulphuret*.

The remaining combinations of columbium have not been sufficiently examined to require notice: the characters of its compounds will be evident from the preceding paragraphs. H. Rose has announced the presence of a new metal in the tantalite of Bavaria, which he has called *Niobium*. (*Ann. Ch. et Ph.*, Mars, 1845.)

§ XXX. MERCURY. Hg. 100.

THE principal ore of this metal is the *sulphuret*, or *native cinnabar*, from which the mercury is separated by distillation with quicklime or iron-filings. Mercury occurs *native*, in small fluid globules, generally dispersed through the sulphuret. It is also found as a *chloride*, *iodide*, and

seleniuret, but these are rare ores: in combination with silver it constitutes *native amalgam*.

Mercury (☿) is a brilliant white metal, having much of the color of silver, whence the terms *hydrargyrum*, *argentum vivum*, and *quicksilver*. It has been known from very remote ages. It is liquid at all common temperatures, solid at -40° , (38.66° HUTCHINS. *Phil. Trans.*, 1783, p. 303,) and contracts considerably at the moment of congelation. Its characters, when frozen, appear to vary with the temperature, being flexible and malleable when verging towards liquefaction, but somewhat brittle at much lower temperatures. Its specific heat is 0.03332. (REGNAULT.) It boils and becomes vapor at about 660° (CRICHTON), 656° (HEINRICH). It emits vapor at all temperatures above 40° , but no apparent spontaneous evaporation goes on from it when below that temperature. (FARADAY.) Its specific gravity at 60° is 13.568. According to Kupfer the density of mercury at 39.2° is 13.5886; at 62.6° , 13.5569; at 78.8° , 13.535. In the solid state its density exceeds 14. (14.39 SCHULZ, *Gehlen's Journ.*, iv. 434: 14.465 BIDDLE, *Phil. Mag.*, xxx. 134. But the exact temperature to which these densities refer does not seem to have been very accurately ascertained.) The specific gravity of mercurial vapor is 6.976. (DUMAS, *Ann. de Ch. et Ph.*, xxxiii.)

Mercury is said to be sometimes adulterated with lead and bismuth, a fraud easily detected by the want of its due fluidity, and by its not being perfectly volatile, but leaving a residuum when evaporated from a platinum or iron spoon. The best method of purifying it is to redistil it in an iron retort, or in an earthen or glass retort, the surface of the mercury being covered with iron filings; but such an operation is rarely necessary, for generally it is extremely pure as it occurs in commerce. When mercury is perfectly pure, it is not affected by exposure to or agitation in contact of air, oxygen, hydrogen, nitrogen, nitrous and nitric oxide, carbonic acid, or alcohol; but when impure it becomes covered with a grey powder when long shaken, which is a mixture of the foreign metallic oxide and finely-divided mercury. When, on the other hand, pure mercury is shaken with water, ether, or oil of turpentine, or rubbed with sulphur, sugar, chalk, lard, conserve of roses, &c., it is reduced, even in a vacuum, to a grey powder, which consists of minute mercurial globules, blended with the foreign body, and when this is abstracted, they again unite into running mercury. In well-made mercurial ointment, these globules are not discernible by the naked eye, being from 1-500th to 1-1000th of a line in diameter. (EHRENBERG, *Poggend.* xxiv. 40.) The mercurial ointment, blue pill, and mercury with chalk, of the *Pharmacopœia*, do not contain a suboxide of mercury, therefore, but are mere mixtures of the different vehicles with mercury in a state of extreme mechanical division. The extent to which this extreme division may be carried is well illustrated in the preparation of which is termed *precipitated mercury*: to obtain it, equal weights of crystallized protochloride of tin and corrosive sublimate may be dissolved, the first in diluted hydrochloric acid, and the second in hot water, and the solutions mixed by stirring: the salt of tin abstracts the whole of the chlorine of the corrosive sublimate, becoming chloride of tin, which remains in solution, while the mercury is liberated, and forms so fine a precipitate that it requires several hours to subside. It may be washed by effusion of hot water and subsidence, and

slightly drained on a filter, but not allowed to dry. (GRAHAM.) Another mode of obtaining mercury in an extraordinary state of division consists in agitating it in dilute sulphuric acid in contact with a few particles of sulphate of copper: in this case electrolytic actions are concerned; metallic copper is first precipitated and then oxidized, and hydrogen is given out upon the mercury, which appears to occasion it to assume the form of *froth*. (DANIELL.) It certainly seems very probable that, although mercury in its ordinary state is quite inactive as a medicine and passes through the bowels unaltered, it may be absorbed, and consequently prove active, when in the extremely comminuted form into which the preceding methods reduce it.

Considerable difference of opinion has prevailed respecting the equivalent or atomic weight of mercury, arising out of the different views which have been adopted in reference to the constitution of its *oxides*, of which there are two, a grey and a red, and both of them salifiable: if the grey be considered as a *protoxide*, and the red a *binoxide*, then the number 200 will represent the metal; if, on the other hand, it be assumed that the *red* oxide is the *protoxide*, and the *grey* a *suboxide* or *dioxide*, the number 100 must be assumed as the weight of the atom of mercury, and there are strong grounds in favor of the latter view; for the grey oxide is very unstable, and deficient, therefore, in the characters of a true protoxide: whereas the red oxide is comparatively permanent and stable, and it is eminently *basic*, verging even upon alkalinity in its properties; and when to these considerations we add the evidence deduced from the connection between the specific heat of mercury and its atomic weight, we are, I think, forced to regard the red oxide of mercury as the protoxide, and notwithstanding the inconvenience that will occasionally ensue in reference to the application of this number to some of the mercurial compounds, to represent the metal by the number 100. (100 GMELIN, THOMSON; 101.266 BERZELIUS; 100.04 ERDMANN and MARCHAND; 101.43 GRAHAM; 202 GREGORY.)

DIOXIDE OF MERCURY. SUBOXIDE OF MERCURY. BLACK OXIDE OF MERCURY. MERCUROUS OXIDE. Hg_2O . This oxide, formerly termed *protoxide*, is obtained when its salts are decomposed by excess of solution of potassa, or when very finely levigated dichloride of mercury (calomel) is triturated with excess of lime water; it must be carefully washed with cold water, and dried at common temperatures under careful exclusion of light. Donovan obtains it by at once adding excess of potassa to calomel diffused through water: if too little potassa be used, the precipitate is resolved into suboxide, protoxide, and metal. (*Ann. Phil.*, xiv.) According to Guibourt, this oxide is never obtained pure, but is always partially resolved, even in the dark, into metal and protoxide. (*Ann. Ch. et Ph.*, i. 422.) By triturating the protoxide with mercury, a mere mixture is the result. The *Ethiops per se* of old pharmacy seems to have been this oxide. Dioxide of mercury, when properly prepared, is a black or brownish black powder, sp. gr. 10.6, (HERAPATH,) easily resolved by the action of light, or when moderately heated, into metal and protoxide. Though insoluble in water, it has a metallic taste. With solution of sal-ammoniac it yields corrosive sublimate and metallic mercury. It consists of

						Thenard.	Donovan.	Seftström.			
Mercury	2	...	200	...	96.15	...	96.16	...	96.04	...	96.2
Oxygen.....	1	...	8	...	3.85	...	3.84	...	3.96	...	3.8
<hr/>											
Dioxide of mercury	1		208		100.00		100.00		100.00		100.0

The salts of this oxide are generally obtained either by its direct solution; or by digesting excess of mercury with the acids or with the salts of the red oxide; or by double decomposition: they are usually yellow when basic, but otherwise white, soluble in water, redden litmus, and taste metallic: some of them are resolved by the action of water into an insoluble basic, and a soluble acid salt. They give black precipitates with the caustic alkalis. With carbonate of potassa they afford yellow, and with bicarbonate white precipitates, sparingly soluble in excess of the precipitant, and becoming black, and losing carbonic acid when boiled. With carbonate of ammonia the precipitate is at first white, but blackens on adding it in excess. With hydrochloric acid and soluble chlorides these salts give a white precipitate of dichloride of mercury, which is immediately blackened by the alkalis. With sulphuretted hydrogen, and the hydrosulphurets, the precipitate is black; with phosphate of soda, white; with iodide of potassium, dirty green, and soluble in excess of the precipitant; with hydrocyanic acid mercury is precipitated, and a cyanide of mercury formed. $\text{Hg}_2\text{O} + \text{HCy} = \text{Hg} + \text{HgCy} + \text{HO}$.

OXIDE OF MERCURY. PEROXIDE OF MERCURY. RED OXIDE OF MERCURY. MERCURIC OXIDE. HgO . This oxide, considered, for the reasons above stated, as a compound of 1 atom of mercury with 1 of oxygen, must be regarded, according to the usual principles of nomenclature, as a protoxide, though hitherto it has generally been assumed as consisting of 1 atom of mercury and 2 of oxygen, and has therefore been termed the *binoxide* or *peroxide*, there being no higher degree of

oxidizement. It is produced, 1. by exposing mercury, heated nearly to its boiling-point, to the action of air. It becomes coated with reddish-brown scales, spangles, and crystals, and is ultimately entirely converted into a red crystallized substance, called in old pharmaceutical works, *precipitatum per se*, or *calcined mercury*. It is the *hydrargyri binoxydum* of the *London Pharmacopœia*. It is most easily obtained in a pure form, by introducing into a flat-bottomed matrass, of the annexed shape*, about 8 ounces of mercury, and placing it in a sand-bath, heated nearly to the boiling-point of the metal. In about a month's time nearly the whole is converted into oxide, air being freely admitted by the tube, while its length pre-



vents the escape of mercurial vapor, which condenses and falls back into the body of the vessel; the remaining portion of running mercury may be driven off by exposing it in a basin to a heat below redness. 2. This oxide may also be obtained by evaporating nitrate of mercury to dryness, and carefully exposing the residue to heat. In this process 25 parts of mercury are dissolved in 35 of nitric acid, nitric oxide is abundantly disengaged, and on evaporation to dryness, a

* This kind of flask or matrass was formerly termed by the French "Boyle's Hell," *Enfer de Boyle* (fig. 325.)

pernitrate of mercury remains, which is carefully heated so long as fumes of nitrous acid are evolved; the resulting oxide is in the form of an orange-red crystalline powder, forming the *Hydrargyri nitrico-oxidum* of pharmacy. (See *Nitrate of Mercury*.) 3. A third mode of obtaining peroxide of mercury consists in adding excess of potassa to a solution of corrosive sublimate, or triturating corrosive sublimate in the alkaline solution: a yellow powder is thus thrown down, which is a *hydrated peroxide*; it loses its water at a moderate heat. If the potassa be not in considerable excess the precipitate is an oxichloride.

Peroxide of mercury has an acrid metallic taste, and is poisonous; it is very sparingly soluble in water, and the solution when exposed to air becomes gradually covered by a brilliant metallic film (DUMAS); it has a metallic taste; it converts the blue infusion of violet-petals to green, and is rendered brown by sulphuretted hydrogen; some chemists deny this solubility of the perfectly pure peroxide, and ascribe its apparent solubility to the presence of a trace of the pernitrate: but the experiments of Anthon and of Marchand confirm its solubility. (*Poggend.*, xlii. 459.) Its specific gravity is 11·074. When this oxide is heated, it acquires a black color, but becomes again red on cooling; at a red-heat it evolves oxygen, and is reduced to the metallic state: it was from this source that Priestley first obtained oxygen gas. When long exposed to light it becomes black upon the surface, in consequence, apparently, of superficial reduction. The peculiarities of the oxide prepared by heat alone, as opposed to those of the precipitated oxide, which have been adverted to by Pelouze and by Gay Lussac (*Comptes Rendus*, xxi. 50 and 309,) seem to depend entirely on mechanical causes, the aggregation probably of the former rendering it less easily acted upon by heat, chlorine, &c. than the latter. It should be entirely volatilized when placed upon a red-hot iron, for it is sometimes adulterated with red lead.

This oxide of mercury is easily decomposed by sulphur, phosphorus, and several of the metals: when mixed with sulphur and heated in a retort it explodes, and with phosphorus it explodes by the blow of a hammer. Heated with potassium, and sodium, and with zinc, tin, and antimony, it is decomposed with ignition. It consists of

	Zaboarda. Rose. Proust. Donovan. Fourcroy. Seftström.									
Mercury.....	1	100	92·59	90	91	92	92·75	92·4	92·68	
Oxygen	1	8	7·41	10	9	8	7·25	7·6	7·32	
Red oxide of mercury }	1	108	100·00	100	100	100	100·00	100·0	100·00	

This oxide combines with the greater number of the acids, and like the dioxide, forms compounds several of which are resolvable into salts with excess of base, and salts with excess of acid; so that the history of the saline combinations of mercury is thus rendered somewhat complex. There is also a great tendency to the formation of double salts among the haloid mercurial compounds; in short mercury is, of all the metals, that which produces the most numerous and complicated series of saline combinations. The salts of the red oxide are, generally speaking, more active and poisonous than those of the black oxide; they mostly redden litmus, and are reduced first to the state of salts of dioxide, and then to metal, by several deoxidizing agents, such as phosphorous and sulphurous acids, protochloride of tin, sugar, &c.

HYDRARGYRATE OF AMMONIA. AMMONIURET OF OXIDE OF MERCURY. When peroxide of mercury is digested in liquid ammonia a pale-yellow compound of the peroxide with 13·6 *per cent.* of ammonia is obtained. (GUIBOUT.) Dr. Kane considers this as a hydrated compound of amide and oxide of mercury $=\text{HgNH}_2 + 2\text{HgO} + 3\text{HO}$; but it may also be regarded as containing 1 atom of peroxide of mercury + 2 of ammonia. This compound, when recently prepared, detonates when smartly struck with a hammer, or when suddenly heated: when slowly heated it is quietly decomposed.

MERCURY AND CHLORINE combine in two proportions, and form a dichloride or subchloride, and a chloride or perchloride of mercury, compounds corresponding in composition with the two oxides, and, therefore, hitherto generally designated as the *protochloride* and *bichloride* of the metal; the old terms *calomel* and *corrosive sublimate* applied to these chlorides, are distinctively convenient.

DICHLORIDE OF MERCURY. SUBCHLORIDE OF MERCURY. CALOMEL. Hg_2Cl . This compound is first mentioned by Crollius, early in the seventeenth century. The first directions for its preparation are given by Beguin, in the *Tyrocinium Chemicum*, published in 1608. He calls it *draco mitigatus*. Several other fanciful names have been applied to it, such as *aquila mitigata*, *manna metallorum*, *panchymagogum minerale*, *sublimatum dulce*, *mercurius dulcis*, &c. It is the *Hydrargyri chloridum* of the *London Pharmacopœia*.

There are several processes by which the dichloride, or calomel, may be obtained: 1. By the action of mercury on corrosive sublimate*. This mode consists in triturating 4 parts of corrosive sublimate with 3 of mercury (and a little water to prevent the dust rising), until the globules disappear, and the whole assumes the appearance of an homogeneous grey powder, which is introduced into a matrass, placed in a sand-heat, and gradually raised to redness. The subchloride sublimes, mixed with a little of the chloride, the greater part of which, however, being more volatile, rises higher in the matrass; that which adheres to the subchloride may be separated, by reducing the whole to a fine powder, and washing in large quantities of hot distilled water. Dichloride, in the form of a dull-white insipid powder, remains. It was formerly the custom to submit this product to very numerous sublimations, under the idea of rendering it *mild*; but these often tended to the production of corrosive sublimate; and the calomel of the first sublimation, especially if a little excess of mercury be found in it, is often more pure than that afforded by subsequent operations. In this process the operation consists in reducing the chloride to the state of dichloride by the addition of mercury; it is objectionable on account of the heat required, and the destruction of the matrasses in which it is sublimed, so that some have proposed to substitute the *humid process*, as it is termed, by precipitation, as devised by Scheele and Chenevix. 2. It is as follows: Form a sub-

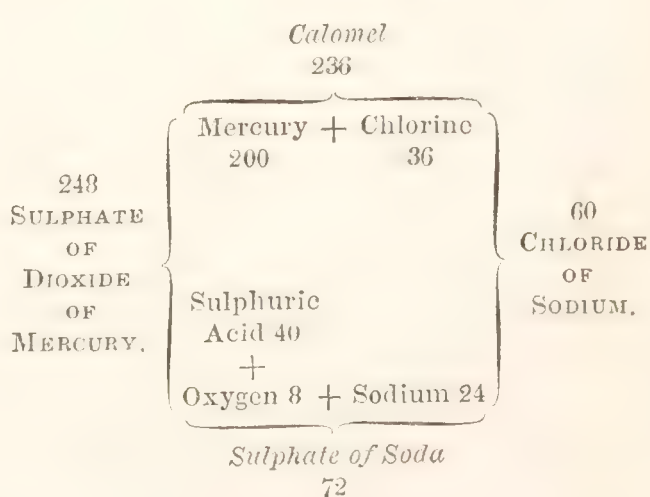
* Dr. A. T. Thomson has a patent for the manufacture of calomel and corrosive sublimate, by directly combining the vapor of mercury with chlorine. (*Chem. Gaz.*, February, 1843.)

nitrate of mercury by dissolving as much mercury as possible in nitric acid; then dissolve in boiling water a quantity of chloride of sodium, equal to half the weight of the mercury used, and render this solution sensibly sour by hydrochloric acid, and pour the hot solution of subnitrate into it. Wash and dry the precipitate. If this process be carefully performed, and the precipitate thoroughlyedulcorated, the calomel is said to be sufficiently pure; but a small portion of chloride of sodium is apt to remain combined with it, which might affect its medical uses.

3. The process by sublimation appears on the whole the least exceptionable for the production of this important article of pharmacy: it is as follows: Boil 2 pounds of mercury with 30 ounces of sulphuric acid in a glass vessel, until the mercuric sulphate is dry. When it has cooled, rub it with 2 pounds of mercury in an earthenware mortar, till they are well mixed. Then add $1\frac{1}{2}$ pounds of chloride of sodium, and rub them together until globules are no longer visible. Put this mixture into a proper vessel, and heat it gradually to redness; the subchloride of mercury, or calomel, sublimes, and condenses in various forms, according to the rapidity of the operation, and the form and capacity of the subliming vessel. If intended for medicinal use, it should be cautiously reduced to an impalpable powder, and washed and levigated with repeated affusions of hot distilled water, till it becomes perfectly tasteless, and till the clear water which filters from the washed powder is not discolored by the addition of an aqueous solution of sulphuretted hydrogen. This process has many advantages over the first method. The mercuric sulphate may be formed by boiling the metal with sulphuric acid to dryness in a cast-iron vessel, which should be conveniently arranged for the escape of the abundant fumes of sulphurous acid developed by the action of the mercury, and which are often a serious nuisance to the neighbourhood: they may be very effectually annihilated by suffering them to pass through a long flue and lofty chimney, mixed with coal smoke. The sulphate is then triturated as above directed with a sufficient quantity of metallic mercury to convert it into a sulphate of the suboxide (or mercurous sulphate), mixed with a due proportion of common salt, and subjected to sublimation. The sulphate of the suboxide is a compound of

1 proportional of dioxide of mercury	=	208
1 " sulphuric acid	=	40
		<hr/>
		248

To convert it into calomel or dichloride of mercury, it is mixed with 1 proportional of chloride of sodium, the chlorine of which combines with the mercury of the oxide to form a dichloride, whilst its sodium becomes sulphate of soda; $\text{Hg}_2\text{O}, \text{SO}_3 + \text{NaCl} = \text{NaO}, \text{SO}_3 + 2\text{Hg}_2\text{Cl}$; as shown in the annexed diagram.



The form in which calomel sublimes depends much upon the dimensions and temperature of the subliming vessels. In small vessels it

generally condenses in a crystalline cake, the interior surface of which is often covered with beautiful quadrangular prismatic crystals (BROOKE, *Ann. of Phil.*, ii. 427, 2nd Series), transparent, and of a texture somewhat elastic or horny: in this state it acquires, by the necessary rubbing into powder, a decidedly yellow or buff tint, more or less deep according to the degree of trituration which it has undergone. If, on the contrary, the calomel be sublimed into a very capacious and cold receiver, it falls in an impalpable and perfectly white powder, which only requires due elutriation to fit it for use; it then remains perfectly white. By a modification of the process, it may be suffered as it sublimes to fall into water, according to Jewell's patent. (On the means of obtaining calomel in impalpable powder, see SOUBEIRAN, *Journ. de Pharm.*, Nov. 1842, and *Chem. Gaz.*, Feb. 1843.) But in whatever state calomel is obtained it requires careful washing as above directed, and extreme care as to its state of minute mechanical division. It was formerly the custom to wash it with solution of sal-ammoniac or of common salt, in order, as it was supposed, the more effectually to deprive it of adhering corrosive sublimate; but in these cases a portion of the calomel was actually decomposed and converted into corrosive sublimate and metallic mercury; so that copious ablution with hot distilled water should only be resorted to. The different aspects under which calomel presents itself, will now be intelligible.

It may be added, that the buff aspect of this substance generally indicates the absence of corrosive sublimate, though it by no means follows, as a consequence, that when snow-white, it contains it. When the surface of massive sublimed calomel is scratched, it always exhibits a buff color: it also becomes yellow when heated, but loses this tint as it again cools.

Calomel should be perfectly tasteless, inodorous, and insoluble in water. Dumas states it to be soluble in 12,000 parts of boiling water; and Graham says it is so insoluble, that when protonitrate of mercury is added to water containing a two hundred and fifty-thousandth part of hydrochloric acid, a sensible precipitate of calomel appears. I have found that, upon pouring distilled water upon pure calomel on a good filter, the liquor which passes is not affected by sulphuretted hydrogen. Many authorities, however, concur in stating that by continuous boiling in water, a portion of corrosive sublimate is eventually formed. Its specific gravity is 7.17 (HASSENFRATZ): 6.9 (KARSTEN): 7.14 (BOULLAY.) At a heat somewhat below redness, it rises in vapor, without previous fusion; but it fuses when subjected to heat under pressure. It emits no vapor at common temperatures, (FARADAY). The density of its vapor is about 8.2; or 119 in reference to hydrogen as unity. When scratched or broken in the dark, it phosphoresces. It is decomposed by the fixed alkalis and by ammonia, and suboxide of mercury is one of the results. Ammoniacal gas blackens calomel, but heat restores the original color, and the calomel is unchanged. By hot hydrochloric acid it is resolved into mercury and corrosive sublimate, but when boiled in dilute hydrochloric acid a portion is dissolved without decomposition. (BOULLAY, *Ann. Ch. et Ph.*, xxxiv. 343; MIALHE, *Journ. de Pharm.*, xxvi.) By nitric acid it is converted into corrosive sublimate and pernitrate, with the evolution of nitric oxide. $3\text{Hg}_2\text{Cl} + 4\text{NO}_5 = 3\text{HgCl} + 3[\text{HgO}, \text{NO}_5]$

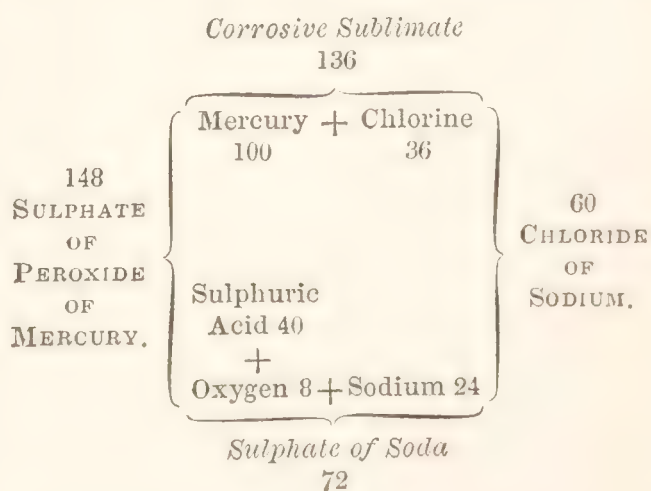
+NO₂. Sulphur, phosphorus, and several of the metals decompose it: thus, when heated with a minimum of sulphur it yields cinnabar and corrosive sublimate; $\text{Hg}_2\text{Cl} + \text{S} = \text{HgS} + \text{HgCl}$; with a maximum of sulphur the products are cinnabar and chloride of sulphur; $\text{Hg}_2\text{Cl} + 4\text{S} = 2\text{HgS} + \text{S}_2\text{Cl}$. (GMELIN.) Heated in the vapor of phosphorus, the products are phosphuret of mercury and chloride of phosphorus. (H. DAVY.) Boiled with copper and water, chloride of copper and metallic mercury are produced. (VOGEL, *Journ. Prakt. Chem.*, viii. 107.) When calomel is triturated with iodine and water, corrosive sublimate and iodide of mercury are formed; $\text{Hg}_2\text{Cl} + \text{I} = \text{HgCl} + \text{HgI}$. With aqueous hydrocyanic acid calomel yields metallic mercury, and cyanide of mercury and hydrochloric acid are found in solution; $\text{Hg}_2\text{Cl} + \text{HCy} = \text{Hg} + \text{HgCy} + \text{HCl}$. Calomel consists of

						Turner.
						Davy.
						Zaboada.
Mercury	2	200	84.75 85
Chlorine	1	36	15.25 15
<hr/>						
Dichloride of mercury.....	1		236		100.00	100

Native Protochloride of Mercury, or *Mercurial Horn Ore*, has been found in Germany, France, and Spain, usually crystallized, and sometimes incrusting and massive: it is rare.

CHLORIDE OF MERCURY. PERCHLORIDE OF MERCURY. BICHLORIDE OF MERCURY. OXYMURIATE OF MERCURY. CORROSIVE SUBLIMATE. HgCl . When mercury is heated in excess of chlorine, it burns with a pale flame, the gas is absorbed, and a white volatile substance rises, which is this chloride. When oxide of mercury is substituted for the metal, oxygen is expelled; $\text{HgO} + \text{Cl} = \text{HgCl} + \text{O}$: and when the oxide is gently heated in hydrochloric gas, water and the chloride are the results; $\text{HgO} + \text{HCl} = \text{HgCl} + \text{HO}$. The mechanical condition of the oxide greatly influences these actions: (See in reference to them, *hypochloric acid*, &c. p. 281.)

The ordinary process for making corrosive sublimate, consists in exposing a mixture of chloride of sodium and sulphate of mercury to heat in a proper subliming-vessel. The sulphate is formed by boiling 2 lbs. of mercury with 30 oz. of sulphuric acid to dryness; it is then rubbed to powder with 4 lbs. of chloride of sodium, and the mixture put into a large flask or into an earthen subliming-vessel, and exposed to a heat gradually raised to redness: *corrosive sublimate* rises, and *sulphate of soda* is the residue; $\text{HgO}, \text{SO}_3 + \text{NaCl} = \text{NaO}, \text{SO}_3 + \text{HgCl}$, as shown in the annexed diagram.



The *sulphate of mercury* is generally prepared upon the large scale by heating the acid and metal in an iron pot, as in the case of calomel,

proper means being adopted to carry off the copious fumes of sulphurous acid arising from the decomposition of a portion of the sulphuric acid, during the peroxidizement of the mercury. The whole is then evaporated to dryness, and the subsequent sublimation is performed in glass, earthenware, or iron vessels, their form and arrangement being much dependent upon the quantity of materials employed.

Chloride of mercury has an acrid nauseous taste, leaving a permanent metallic and astringent flavor upon the tongue: it is a powerful corrosive poison. It evaporates to a small extent at common temperatures. (FARADAY.) Its specific gravity is 5·2 (HASSENFRATZ): 5·4 (KARSTEN): 5·42 (BOULLAY). It is usually met with in the form of white semi-transparent and imperfectly-crystallized masses; or in powder. It frequently exhibits prismatic crystals upon the inner surfaces of the sublimed cakes. (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 285.) It is soluble in about 16 parts of cold, and 3 of hot water, (18·5 of water at 60°, and 2 to 3 of water at 212°. J. DAVY), and as the solution cools, it deposits quadrangular prismatic crystals: it is more copiously soluble in alcohol, 7 parts of which at 60° dissolve 3, and at its boiling-point 6, of corrosive sublimate: it is also soluble in ether, which, at common temperatures, takes up about one-third its weight; and when ether is agitated with the aqueous solution, it abstracts the perchloride from the water: it is also soluble in volatile oils. According to Gmelin, it dissolves in 3 parts of alcohol and in 4 of ether. When heated, it readily fuses, boils, and entirely sublimes in the form of a dense white vapor, powerfully affecting the nose and mouth: the density of its vapor is 9·4; 1 volume of it including 1 volume of mercury-vapor and 1 volume of chlorine. It is nearly insoluble in concentrated nitric and sulphuric acids. Hydrochloric acid of the specific gravity 1·158, at the temperature of 60°, dissolves about its own weight, and the solution, when cooled to about 40°, concretes into a mass of acicular crystals; there appear to be two or three of these definite *hydrochlorates of chloride of mercury*; they are partially decomposed when added to great excess of water, and resolved into free hydrochloric acid and chloride.

When solution of chloride of mercury is decomposed by potassa, soda, or lime, a yellow precipitate is thrown down, which, when the alkali is in excess, is a hydrated *oxide of mercury*. Such a mixture of a pint of lime-water with a drachm of corrosive sublimate is used as an external application, under the name of *Aqua phagedænica*, or *red lotion*. It is in fact a solution containing undecomposed corrosive sublimate and chloride of calcium, mixed with oxide, or with oxichloride, of mercury. For the entire decomposition of 1 atom of corrosive sublimate = 136, 1 atom of lime is required = 28: and the results are 1 atom of oxide of mercury = 108, and 1 of chloride of calcium = 56: or $\text{HgCl} + \text{CaO} = \text{HgO} + \text{CaCl}$. When calomel is similarly decomposed, black or suboxide of mercury is thrown down, and the mixture was formerly known in pharmacy under the name of *black lotion*: in this case 1 atom or equivalent of calomel = 236, being decomposed by 1 of lime = 28, the results are 1 atom of suboxide of mercury = 208, and 1 of chloride of calcium = 56: or $\text{Hg}_2\text{Cl} + \text{CaO} = \text{Hg}_2\text{O} + \text{CaCl}$. When in these cases of decomposition of calomel, an aqueous solution of ammonia is substituted for that of lime, or of the fixed alkalis, one half of its chlorine is converted into sal-

ammoniac, and a dark grey powder results, which is a compound of subchloride and subamidide of mercury; $2\text{NH}_3 + 2\text{Hg}_2\text{Cl} = \text{NH}_4\text{Cl} + [\text{Hg}_2\text{Cl} + \text{Hg}_2\text{NH}_2]$. KANE. The corresponding decomposition of corrosive sublimate will be noticed in a subsequent paragraph. When calomel, or corrosive sublimate, is heated to redness with the fixed alkalis, the results are mercury, oxygen, and a chloride of the alkaline metal: thus, in respect to calomel, $\text{Hg}_2\text{Cl} + \text{KO} = 2\text{Hg} + \text{O} + \text{KCl}$; and with corrosive sublimate, $\text{HgCl} + \text{KO} = \text{Hg} + \text{O} + \text{KCl}$.

Corrosive sublimate is either decomposed by, or combines with, the greater number of organic bodies; some of them convert it into calomel, by the abstraction of chlorine; others enter into more complicated combinations, some of which are remarkably permanent; the applications of it to the preservation of anatomical preparations, and to the prevention of dry rot, illustrate these actions, and will again be alluded to under organic bodies: hence also the efficacy of a mixture of white of egg and water, in preventing or mitigating the poisonous effects of corrosive sublimate in the stomach.

Corrosive sublimate consists of

					Davy. Turner.
Mercury	1	...	100	...	73.53
Chlorine	1	...	36	...	26.47
<hr/>					
Chloride of mercury	1		136		100.00

OXICHLORIDE OF MERCURY. $\text{HgCl}, 3\text{HgO}$. It has been stated that when a solution of corrosive sublimate is decomposed by excess of potassa or soda, a hydrated peroxide of mercury is thrown down; but if the mercurial salt remain in excess, the precipitate is then of a brown color, and contains oxide and bichloride of mercury; when the alkaline carbonates are used, there are the same general results; but with bicarbonate of potassa or of soda, there is no immediate precipitate, so that a solution of corrosive sublimate may be employed to detect the presence of neutral alkaline carbonate in those bicarbonates. Oxichloride of mercury may also be formed by passing chlorine through a mixture of water and oxide of mercury; in this way, 100 parts of the oxide yield about 58 of a brown crystallized powder. It may also be obtained crystalline, and of a very dark color, by mixing solutions of corrosive sublimate and chloride of lime, and boiling the liquid; or by treating a solution of corrosive sublimate with bicarbonate of potassa, and allowing the solution to stand in an open vessel, when carbonic acid gradually escapes, and oxichloride is deposited. It is also formed by boiling a solution of corrosive sublimate with carbonate of lime. This oxichloride is decomposed by a moderate heat; chloride of mercury sublimes, and the red oxide is left. Mixed with potassa and heated to redness, the products are oxygen gas, mercury, and chloride of potassium. It is very sparingly soluble in cold water; somewhat more soluble in boiling water, which, on cooling, deposits dark-brown crystalline grains. Its components are

					Phillips.	Soubeiran.	Thaulow.
Mercury	4	...	400	...	86.95	86.58	87.50
Chlorine	1	...	36	...	7.82	6.85	7.12
Oxygen	3	...	24	...	5.23	6.57	5.38
<hr/>							
Oxichloride of mercury	1		460		100.00	100.00	100.00

AMMONIOCHLORIDE OF MERCURY. $\text{NH}_3, 2\text{HgCl}$. When corrosive sublimate is heated in a stream of ammoniacal gas, a white crystalline, volatile, and fusible compound is obtained, which is not soluble in water without decomposition. (H. ROSE, *Poggend.*, xx. 158.) According to Mitscherlich a similar compound is obtained by heating a mixture of red oxide of mercury and sal-ammoniac. Kane and Gmelin have suggested various formulæ by which it may be represented: the simplest view of its composition is

						H. Rose.
Ammonia	1	...	17	...	5.89	6.37
Chloride of mercury	2	...	272	...	94.11	93.63
<hr/>						
Ammoniochloride of mercury	1		289		100.00	100.00

HYDRARGOCHLORIDE OF AMMONIUM. SAL ALEMBROTH. $\text{NH}_4, \text{Cl} + \text{HgCl}$. When a solution containing 1 atom of sal-ammoniac and 1 of corrosive sublimate in a small quantity of water is carefully evaporated, it yields rhombic and acicular prisms: they dissolve in 0.66 of water at 50° , and are much more soluble in boiling water: they are permanent in the air, but when dried at 212° , become opaque, and lose about 5.5 per cent. of water. The components of the anhydrous salt are

Chloride of ammonium	1	...	54	...	28.42
Chloride of mercury	1	...	136	...	71.58
<hr/>					
Hydrargochloride of ammonium	1		190		100.00

When 1 atom of sal-ammoniac and 2 of corrosive sublimate are intimately mixed and duly heated, a compound = $\text{NH}_4, \text{Cl} + 2\text{HgCl}$ sublimes: when the same salts are dissolved in water, the solution yields, on evaporation, long silky acicular crystals = $\text{NH}_4, \text{Cl} + 2\text{HgCl} + \text{HO}$.

AMIDOCHLORIDE OF MERCURY. $\text{HgNH}_2, \text{HgCl}$. Obtained by adding slight excess of ammonia to a solution of corrosive sublimate, washing the precipitate with a little cold water, and drying it by a gentle heat: $2\text{HgCl} + 2\text{NH}_3 = \text{HgNH}_2, \text{HgCl} + \text{NH}_4, \text{Cl}$. It is a white powder, which when heated to redness, is resolved into calomel, nitrogen, and ammonia. $3[\text{HgNH}_2, \text{HgCl}] = 3[\text{Hg}_2 \text{Cl}] + \text{N} + 2\text{NH}_3$. Boiled in water it is converted into sal-ammoniac, which is dissolved, and an almost insoluble yellow powder, which is a compound of amidide, chloride, and oxide of mercury: $2[\text{HgNH}_2, \text{HgCl}] + 2\text{HO} = \text{NH}_4\text{Cl} + [\text{HgNH}_2 + \text{HgCl} + 2\text{HgO}]$ (KANE, *Trans. R. Irish Acad.*, xvii.) The components of the above white precipitate are

Mercury	2	...	200	...	79.38
Nitrogen	1	...	14	...	5.56
Hydrogen.....	2	...	2	...	0.79
Chlorine	1	...	36	...	14.27
<hr/>					
Amidochloride of mercury	1		252		100.00

This compound is the *Hydrargyri ammonio-chloridum* of the *London Pharmacopœia*, and is considered by Phillips as composed of 1 equivalent of corrosive sublimate, 1 of oxide of mercury, and 1 of ammonia. (*Translation Lond. Pharm.*) By Hennel (*Quart. Journ. Science*), and Mits-

cherlich (*Ann. Ch. et Ph.*, xxxv. 428,) it is represented as a compound of 1 equivalent of oxide of mercury, and 1 of sal-ammoniac; but the existence of oxygen in the dry compound has certainly not been satisfactorily proved.

AMIDOCHLORIDE OF MERCURY WITH CHLORIDE OF AMMONIUM. $\text{Hg}, \text{NH}_2, \text{HgCl} + \text{NH}_4 \text{Cl}$. This is the white powder which falls on adding carbonate of potassa or soda (not in excess) to a cold aqueous solution of equal parts of corrosive sublimate and sal-ammoniac: it is the "white precipitate" and *calx hydrargyri alba* of former Pharmacopœiæ: it is not decomposed by boiling water, and fuses when heated, giving off ammonia and nitrogen, whilst a mixture of calomel, corrosive sublimate, and sal-ammoniac sublimes. (KANE, *Elem. Chem.*, 837.) Its components are stated to be

						Kane.
Mercury	2	200	65·36 65·81
Nitrogen	2	28	9·11 8·96
Hydrogen	6	6	1·96 1·92
Chlorine	2	72	23·57 22·57
<hr/>						
Amidochloride of ammonium and mercury	1		306		100·00	99·26

These preparations are sometimes adulterated with sulphate of lime, and carbonate of lead, impurities which are detected by their want of volatility at a red-heat: their only use is in pharmacy, being applied chiefly in the form of ointment in certain diseases of the skin: they are also employed for the destruction of lice.

HYDRARGOCHLORIDE OF POTASSIUM. CHLORHYDRARGYRATE OF POTASSIUM. KCl, HgCl . When excess of corrosive sublimate is added to a solution of chloride of potassium, the addition of alcohol to the mixed solution causes the separation of silky crystals: their aqueous solution yields right rhombic prisms, composed, according to Bonsdorff (*Ann. Ch. et Ph.*, xlv.; *Poggend.*, xvii. 123), of

						Bonsdorff.
Chloride of potassium	1	76	34·39 33·73
Chloride of mercury	1	136	61·53 61·31
Water	1	9	4·00 4·96
<hr/>						
Hydrargochloride of potassium....	1		221		100·00	100·00

By dissolving in water the crystals which are deposited from a solution of corrosive sublimate in strong cold hydrochloric acid, and then saturating with potassa, silky acicular crystals are deposited, difficultly soluble in alcohol, but very soluble in water $= \text{KCl}, 2\text{HgCl}$. (BOULLAY. *Ann. Ch. et Ph.*, xxxiv. 344.) They contain

						Bonsdorff.
Chloride of potassium	1	76	20·77 20·97
Chloride of mercury	2	272	74·32 75·24
Water	2	18	4·91 3·79
<hr/>						
Bihydrargochloride of potassium	1		366		100·00	100·00

When a boiling solution of corrosive sublimate in hydrochloric acid is saturated with potassa and cooled, it deposits silky crystals containing $\text{KCl}, 4\text{HgCl}$. (BOULLAY.) The same salt is obtained by agitating a hot

aqueous solution of chloride of potassium with powdered corrosive sublimate; on cooling, the liquor concretes into a crystalline mass: the crystals are easily soluble in warm water, but less so in alcohol. They contain

Chloride of potassium	1	...	76	...	11.58
Chloride of mercury	4	...	544	...	82.91
Water	4	...	36	...	5.51
<hr/>					
Quadrihydrargochloride of potassium	1		656		100.00

In these compounds it is assumed that the relation of the mercuric chloride to the chloride of potassium, is that of acid to base.

HYDRARGOCHLORIDE OF SODIUM. By agitating pulverised corrosive sublimate in a saturated solution of chloride of sodium, and leaving the filtered liquor to spontaneous evaporation, groups of delicate six-sided prisms are formed = NaCl,2HgCl,3HO. They are permanent, soluble in 0.3 of water at 60°, and fusible at 212° in their water of crystallization. (BONSDORFF.) Their aqueous solution is precipitated by the alkalis in the same way as corrosive sublimate. When agitated with ether the corrosive sublimate is not abstracted by that liquid, but it takes up the double salt in the proportion of 1 part to 275 of ether. (LASSAIGNE, *Ann. Ch. et Ph.*, LXIV. 104.)

A solution of 7 parts of common salt in 20 of water dissolves 32 parts of corrosive sublimate (at 60°), and 35 parts when gently heated; its specific gravity is then 2.14. (J. DAVY.) The salt NaCl,HgCl is not crystallizable. (BONSDORFF.) The above-mentioned crystals contain

						Schindler.	Bonsdorff.
Chloride of sodium	1	...	60	...	16.71	16.10	16.0
Chloride of mercury	2	...	272	...	75.82	75.86	75.0
Water	3	...	27	...	7.47	7.73	8.8
<hr/>							
Bihydrargochloride of sodium	1		359		100.00	99.69	99.8

HYDRARGOCHLORIDE OF CALCIUM. CaCl,5HgCl. When a strong solution of chloride of calcium is saturated with corrosive sublimate and evaporated, it deposits octohedral crystals, somewhat deliquescent, and which are decomposed by cold water so as to become opaque from the superficial separation of corrosive sublimate; but when heat is applied the resulting solution again yields similar crystals to those originally formed, and consisting of

						Bonsdorff.
Chloride of calcium.....	1	...	56	...	6.93	6.65
Chloride of mercury	5	...	680	...	84.16	85.23
Water	8	...	72	...	8.91	8.12
<hr/>						
Hydrargochloride of calcium	1		808		100.00	100.00

When the mother-liquor of the above salt is further evaporated, it yields acicular crystals, which by a second solution and evaporation at 90° may be obtained in rhombic tables, very deliquescent, and apparently = CaCl,2HgCl,6HO. (BONSDORFF.)

HYDRARGOCHLORIDE OF BARIUM. BaCl,2HgCl. A cold saturated

solution of chloride of barium shaken with pulverized corrosive sublimate and filtered, at first deposits crystals of corrosive sublimate, and afterwards those of the double salt in small rhombic prisms and tables which slightly effloresce in dry air. (BONSDORFF. *Poggend.*, xvii. 130.) They consist of

						Bonsdorff.
Chloride of barium	1	105	26.58 28.67
Chloride of mercury	2	272	68.86 65.73
Water.....	2	18	4.56 5.60
<hr/>						
Hydrargochloride of barium	1		395		100.00	100.00

20 parts of water saturated at 60° with 8.7 parts of crystallized chloride of barium, dissolve 20 parts of corrosive sublimate when gently heated: the specific gravity of the solution is 1.9, and it deposits small cubic crystals. (J. DAVY, *Phil. Trans.*, 1822, 364.)

HYDRARGOCHLORIDE OF STRONTIUM may be obtained in the form of acicular crystals, permanent in the air.

HYDRARGOCHLORIDE OF MAGNESIUM. A saturated solution of corrosive sublimate and chloride of magnesium yields on careful evaporation two sets of crystals; those which are first deposited are = $MgCl, 3HgCl, 5HO$; they are flat rhombic prisms, permanent in the air, and by the first action of water become milky, but afterwards dissolve and may again be obtained by evaporation. When the mother-liquor is evaporated in vacuo, extremely deliquescent rhombic prisms are formed, having the formula $MgCl, HgCl, 6HO$. (BONSDORFF.)

HYDRARGOCHLORIDE OF MANGANESE. Solution of protochloride of manganese saturated by corrosive sublimate and evaporated in vacuo over oil of vitriol, first deposits crystals of corrosive sublimate, and then pale red transparent rhombic prisms, efflorescent in vacuo, but deliquescent in damp air: their formula is $MnCl, HgCl, 4HO$. (BONSDORFF.)

HYDRARGOCHLORIDE OF IRON. Aqueous solution of chloride of iron dissolves corrosive sublimate, and on evaporation in vacuo a portion of the latter salt separates, and then rhombic prisms isomorphous with the manganese salt are formed, which deliquesce in the air and deposit a brown powder: they are = $FeCl, HgCl, 4HO$. (BONSDORFF.)

HYDRARGOCHLORIDE OF ZINC. The mixed solution of chloride of zinc and mercury first deposits crystals of corrosive sublimate, and then a very deliquescent double salt. (BONSDORFF.)

HYDRARGOCHLORIDE OF TIN. $SnCl, Hg_2Cl$. The pulverized amalgam of 3 parts of tin and 1 of mercury is mixed with 24 parts of calomel and heated in a sufficiently capacious glass retort up to about 480°, when a sudden action ensues, and on breaking the retort when cold, a bulky grey compound is obtained, together with metallic mercury: the former is pulverized and heated in a flat-bottomed flask in a bath of fusible metal, so that its temperature may not exceed the boiling-point of mercury, till

white fumes no longer arise; bichloride of tin is first evolved; a sublimate is then obtained of *hydrargochloride of tin*, and protochloride of tin and mercury remain: the sublimate is removed on carefully cutting the flask asunder: it is in the form of small white arborescent crystals, and when heated up to its point of vaporization is partially decomposed: it is decomposed by water into mercury, calomel, and chloride of tin. (CAPITAINE. *Journ. de Pharm.*, xxv. 549.) It consists of

					Capitaine.
Tin	1	...	59	...	17·82
Mercury	2	...	200	...	60·42
Chlorine	2	...	72	...	21·76
<hr/>					
Hydrargochloride of tin	1		331		100·00
					100 0

HYDRARGOCHLORIDE OF COBALT. On evaporating a mixed aqueous solution of chloride of cobalt and corrosive sublimate, red prismatic and deliquescent crystals are obtained isomorphous with the corresponding double salts of manganese and iron. (BONSDORFF.)

HYDRARGOCHLORIDE OF NICKEL, obtained as the preceding, forms deliquescent oblique rhombic prisms. (BONSDORFF.)

HYDRARGOCHLORIDE OF COPPER. On evaporating a solution of corrosive sublimate and chloride of copper, the double salt forms groups of acicular crystals, permanent in the air. When a mixed solution of chloride of copper and hydrargochloride of potassium is spontaneously evaporated, green rhombic prisms are obtained $= 3[\text{KCl}, \text{HgCl}] + \text{CuCl} + 2\text{HO}$; they deliquesce in humid air, and may be dissolved in boiling water and recrystallized by slow evaporation; but if the solution be suddenly cooled, hydrargochloride of potassium separates, leaving a blue solution. (BONSDORFF. *Poggend.*, xxxiii. 81.)

CHLORIDE OF MERCURY AND CHROMATE OF POTASSA. A mixture of 1 atom of corrosive sublimate and 1 of chromate of potassa dissolved in hot water yields, on cooling, groups of red prismatic crystals; ether abstracts the chloride and leaves the chromate, without destroying the form of the crystals. Their formula is $2\text{HgCl} + \text{KO}, \text{CrO}_3$.

CHLORATES OF MERCURY. Chloric acid dissolves both the oxides of mercury; the chlorate of the suboxide has the appearance of a yellowish granular powder, sparingly soluble in hot water, and of a mercurial taste. The chlorate of the peroxide forms white acicular crystals, having the acid flavor of the chloride, and soluble in 4 parts of water at 60° . (VAUQUELIN. *Ann. de Ch.*, xcv.)

A solution of recently precipitated black oxide of mercury in chloric acid, when evaporated over sulphuric acid in vacuo, yields brilliant prismatic crystals $= \text{Hg}_2 \text{O}, \text{ClO}_5$, becoming dull by exposure, and soluble in water and alcohol; they give off oxygen at 482° , forming red oxide and corrosive sublimate; the latter is expelled at 563° , while the oxide remains under 698° . This salt explodes violently under percussion with combustibles. By dissolving red oxide of mercury in chloric acid, and evaporating on a water-bath, octohedral crystals of its chlorate are obtained

$= \text{HgO}, \text{ClO}_5$; triturated with combustibles this salt inflames them without explosion. It is decomposed by water into an acid and basic chlorate. (WAECHTER.)

SUBIODIDE OF MERCURY. PROTIODIDE OF MERCURY. Hg_2I . This compound is obtained, 1. By triturating together 200 parts of mercury and 126 parts of iodine, moistened with alcohol. 2. By adding iodide of potassium to a dilute solution of acetate or nitrate of suboxide of mercury: $\text{Hg}_2\text{O}, \text{NO}_5 + \text{KI} = \text{Hg}_2\text{I} + \text{KO}, \text{NO}_5$. 3. By digesting in boiling water 236 parts of calomel with 166 of iodide of potassium: $\text{Hg}_2\text{Cl} + \text{KI} = \text{Hg}_2\text{I} + \text{KCl}$. 3. By triturating together 1 equivalent of mercury with 1 of iodide of mercury, moistened with alcohol.

Subiodide of mercury is a dingy-green powder; specific gravity 7·6 to 7·7: it is nearly insoluble in water, and insoluble in alcohol. When rapidly heated in a glass tube, it fuses, and sublimes unaltered: gently heated, or long exposed to light, it is resolved into mercury and iodide: it also undergoes the same decomposition by the action of hydriodic acid and the basic iodides, and, when aided by heat, by hydrochloric acid and the basic chlorides. It consists of

Mercury	2	200	61·5
Iodine	1	126	38·5
<hr/>					
Subiodide of mercury	1		326		100·0

YELLOW IODIDE OF MERCURY. Hg_4I_3 . When iodide of potassium is poured into an acid solution of nitrate of mercury, the resulting precipitate is, under careful management, yellow, and consists chiefly of this iodide; but if too much acid be used, it is of a reddish tinge from the presence of periodide, which, however, may be removed by digesting the precipitate in alcohol. The yellow iodide of mercury is more certainly obtained by precipitating the nitrate by a sesquiodide of potassium, made by dissolving half an equivalent of iodine with 1 equivalent of iodide of potassium: it then falls in the form of a yellow precipitate, which when washed with alcohol is free from periodide. This iodide is a yellow powder, which by the action of dilute nitric acid is converted into periodide, so that the precipitate which falls when iodide of potassium is added to the nitrate of mercury, varies in composition with the state of the mercurial salt: if neutral, the green subiodide falls; if slightly acid, the yellow iodide; if very acid, the red periodide. When this iodide is heated, it becomes red, but again yellow on cooling. It consists of

						Boullay.
Mercury	4	400	51·5	51·9
Iodine	3	378	48·5	48·1
<hr/>						<hr/>
Yellow iodide of mercury	1		778		100·0	100·0

IODIDE OF MERCURY. PERIODIDE OF MERCURY. HgI . This compound (sometimes termed *biniodide*, or *red iodide of mercury*), is obtained, 1. By triturating 1 equivalent of mercury with 1 of iodine, (100 mercury and 126 iodine) moistened with a very little water or alcohol. 2. By the mutual decomposition of corrosive sublimate and iodide of potassium.

$\text{HgCl} + \text{KI} = \text{HgI} + \text{KCl}$. When a solution of iodide of potassium is gradually added to one of corrosive sublimate, a red precipitate forms, which redissolves on agitation; it is a soluble compound of chloride and iodide of mercury; on the further addition of iodide of potassium a pale reddish and permanent precipitate is obtained which is also a compound of chloride and iodide, containing, however, more of the latter; this precipitate, on continuing the addition of the iodide of potassium, becomes of a brilliant scarlet, and this is iodide of mercury, but if excess of iodide be added, it disappears, and a colorless solution of hydrargoioidide of potassium is formed; so that to obtain a pure iodide of mercury the relative atomic equivalents must be strictly preserved. This red iodide when dissolved to saturation in a hot solution of iodide of potassium or iodide of zinc, is deposited on cooling in small crystals having the form of an octohedron with a square base, or its modifications: its specific gravity is 6.2 to 6.3. When heated it becomes yellow, and fuses into an amber-colored fluid, giving off vapor which condenses in yellow rhombic plates, which if scratched or ruptured resume a scarlet color; this dimorphism of iodide of mercury has been microscopically examined and well described by Warington. (*Mem. Ch. Soc.*, i. 85.) Iodide of mercury is very sparingly soluble in water, in boiling alcohol, and in ether: it dissolves in hydrochloric and hydriodic acid, and in the aqueous solutions of several ammoniacal salts, and of chloride of potassium. It consists of

Mercury.....	1	...	100	...	44.25
Iodine	1	...	126	...	55.75
<hr/>					
Iodide of mercury....	1		226		100.00

When 1 equivalent of iodide of mercury is fused with 3 of oxide of mercury a compound is formed, which, when subjected to the action of gaseous ammonia, gives off water and leaves a brown substance which is a compound of amidide, iodide, and oxide of mercury ($3\text{HgO}, \text{HgI} + \text{NH}_3 = \text{HgNH}_2, \text{HgI}, 2\text{HgO} + \text{HO}$.) (RAMMELSBERG.) Iodide of mercury absorbs gaseous ammonia, forming a white powder $= \text{HgI}, \text{NH}_3$, which, however, when exposed to air, gradually reddens and loses the ammonia it had absorbed. In aqueous ammonia the iodide also becomes white and forms $2\text{HgI}, \text{NH}_3$; but this, like the preceding compound, is not permanent in the air. When the iodide is boiled in the solution of ammonia, the same compound is obtained in long white needles, and according to Rammelsberg the solution contains iodide of ammonium and iodide of mercury; but, as Berzelius remarks, iodide of ammonium cannot have been formed without the simultaneous production either of oxide or of amidide of mercury.

HYDRARGOIODIDE OF AMMONIUM. $\text{NH}_4\text{I}, 2\text{HgI}$. When 1 atom of sal-ammoniac and 3 of iodide of mercury are boiled together in water, a part of the iodide is deposited as the solution cools, and the remaining liquor yields yellow needles of the above salt; they are permanent in the air, and when fused lose a little water and form a red liquid which concretes into a crystalline mass, at first yellow, but gradually becoming red: at a higher temperature it in part sublimes, and part is decomposed. It may be dissolved in a small quantity of water with little decomposition; with more water about half the mercurial iodide separates, and the remaining

liquor again deposits crystals of the original salt, so that sal-ammoniac remains in solution, and the compound $\text{NH}_4\text{I}, \text{HgI}$, cannot be obtained in the crystalline form. (BOULLAY. *Ann. Ch. et Ph.*, xxxiv. 345.) The above crystals are soluble in alcohol and in ether: they contain

						Boullay.
Iodide of ammonium.....	1	144	23.45 24.3
Iodide of mercury.....	2	452	73.62 71.9
Water	2	18	2.93 3.8
<hr/>						<hr/>
Crystallized hydrargoioidide of ammonium	1		614		100.00	100.0

HYDRARGOIODIDE OF POTASSIUM. $\text{KI}, 2\text{HgI}$. This salt is best obtained by dissolving iodide of mercury in aqueous solution of iodide of potassium; when saturated, it contains $\text{KI}, 3\text{HgI}$, but on slow cooling red crystals of the salt with 2HgI , are deposited, which are isomorphous, when slowly formed, with those of the preceding ammonium-salt: they may also be obtained by boiling iodide of mercury in solution of potassa: oxide of mercury is formed, and, on cooling, iodide of mercury first crystallises, and afterwards, the above hydrargoioidide. $4\text{HgI} + \text{KO} = \text{HgO} + \text{HgI} + [\text{KI}, 2\text{HgI}]$

HYDRARGOIODIDE OF SODIUM. When a cold aqueous solution of iodide of sodium is saturated with iodide of mercury and evaporated in vacuo over oil of vitriol, it yields yellow rhombic prisms, which are very deliquescent. (BONSDORFF. *Poggend.*, xvii. 226.) According to Boullay, 1 atom of iodide of sodium dissolved in a little water, dissolves when heated about 3 atoms of iodide of mercury, 1 atom of which falls on cooling, and on evaporation no crystals, but a yellow mass $= \text{NaI}, 2\text{HgI}$, is obtained, which, when scratched, becomes red, as is the case with the yellow iodide of mercury. This salt is decomposed by water, and on filtering the solution, deliquescent acicular crystals may be obtained from it by evaporation in vacuo, which are $= \text{NaI}, \text{HgI}$.

HYDRARGOIODIDE OF BARIUM. Iodide of mercury is also soluble in warm solution of iodide of barium, and compounds similar to the preceding are formed. Boullay has also described *Hydrargoioidides of Strontium, Calcium, Magnesium, Zinc, and Iron*.

IODATES OF MERCURY. Iodic acid, or iodate of potassa, or of soda, form a white and somewhat crystalline precipitate in a solution of nitrate of suboxide of mercury $= \text{Hg}_2\text{O}, \text{IO}_5$. This salt is anhydrous, and little soluble in water; it is resolved by heat into oxygen gas, mercury, and iodide of mercury: it dissolves in dilute hydrochloric acid, with the evolution of chlorine: it is difficultly soluble in nitric acid. (RAMMELSBERG. *Poggend.*, xlv. 570.)

The persalts of mercury are not precipitated either by iodic acid or iodate of soda, but recently precipitated and moist red oxide of mercury, when heated in aqueous iodic acid, is converted into a white iodate $= \text{HgO}, \text{IO}_5$: the acid does not act upon the red oxide of mercury prepared by heat. This iodate is anhydrous, and is decomposed by heat into oxygen and iodide of mercury: it consists of

						Rammelsberg.
Oxide of mercury	1	108	39.42 39.83
Iodic acid	1	166	60.58 60.17
<hr/>						<hr/>
Iodate of mercury	1		274		100.00	100.00

PERIODATES OF MERCURY. Periodate of soda gives a yellow precipitate in the nitric solution of suboxide, and a white precipitate in that of the oxide of mercury: the former becomes brown, and the latter yellow, when heated; both are readily soluble in dilute nitric acid. (BENCKISER. *Ann. der Pharm.*, xvii. 259.)

DIBROMIDE OF MERCURY. **SUBBROMIDE OF MERCURY.** Hg_2Br_2 is obtained when 1 atom of mercury and 1 of bromide of mercury are thoroughly mixed and heated; it forms a crystalline sublimate of a pale yellow color: it is also thrown down in the form of a white powder on mixing solutions of bromide of potassium and nitrate of suboxide of mercury. Its sp. gr. is 7.3. (KARSTEN.) It is tasteless, insoluble in water, fusible, and volatile at a dull red-heat. With solution of potassa, it yields bromide of potassium and suboxide of mercury: by a boiling solution of hydrobromate or hydrochlorate of ammonia, it is resolved into mercury and soluble bromide. It consists of

Mercury.....	2	200	71.9
Bromine.....	1	78	28.1
<hr/>					
Dibromide of mercury	1		278		100.0

BROMIDE OF MERCURY. **PERBROMIDE OF MERCURY.** HgBr_2 is formed by triturating mercury with bromine; heat, but no light, is evolved; it is also formed when bromine and mercury are shaken together in water; and by digesting oxide of mercury in aqueous hydrobromic acid. It is deposited from its aqueous solution in lamellar crystals, fusible, and volatile: sp. gr. 5.9. (KARSTEN.) It is soluble in 94 parts of water at 48° , and in 4 or 5 of boiling water: its aqueous solution reddens litmus. It is very soluble in alcohol and in ether. It is not decomposed by sulphuric acid. (H. ROSE. *Analyt. Chem.*) But according to Balard, when heated with nitric or with sulphuric acid, bromine is evolved. It consists of

Mercury	1	100	56.18
Bromine	1	78	43.82
<hr/>					
Bromide of mercury	1		178		100.00

An *oxibromide of mercury* $= \text{HgBr}_2 \cdot 3\text{HgO}$, is formed by boiling bromide and oxide of mercury together in water; it is a yellow crystalline powder, sparingly soluble in boiling water; soluble according to Löwig, but according to Rammelsberg insoluble in water. It contains 80 *per cent.* of mercury. (RAMMELSBURG.)

HYDRARGOBROMIDE OF AMMONIUM. When bromide of mercury is gently heated in aqueous ammonia, it absorbs not more than 3.4 *per cent.*; water abstracts hydrobromate of ammonia from this compound, and leaves a yellow powder, which evolves ammonia when acted on by sulphuret of potassium. (ROSE, and RAMMELSBURG. *Poggend.*, xx. and lv.)

Ammonia throws down a white amidobromide from the aqueous solution of bromide of mercury $= \text{HgNH}_2 + \text{HgBr}$: it is insoluble in water and in alcohol, and only sparingly soluble in ammonia: gently heated, it yields ammonia, and a sublimate $= \text{NH}_3, 2\text{HgBr}$, the residue being $= \text{Hg}_3\text{N}, 2\text{HgBr}$. (MITSCHERLICH.) $6 [\text{HgNH}_2, \text{HgBr}] = 3\text{NH}_3 + [\text{NH}_3, 2\text{HgBr}] + 2 [\text{Hg}_3\text{N}, 2\text{HgBr}]$. (GMELIN.)

Bromide of mercury is abundantly soluble in aqueous solution of hydrobromate of ammonia: the carbonated alkalis throw down the preceding compound of amide and bromide of mercury when added to this solution. (LÖWIG.)

HYDRARGOBROMIDES OF POTASSIUM. When a cold and moderately concentrated solution of bromide of potassium is saturated with bromide of mercury, and evaporated, crystals are formed $= \text{KBr}, 2\text{HgBr}$. When 1 atom of this salt and 1 of bromide of potassium are dissolved together in water, the solution yields, on evaporation, prismatic crystals $= \text{KBr}, \text{HgBr}$. (BONSDORFF. *Poggend.*, xix. 339.)

Hydrargobromides of Sodium, Barium, Calcium, and Magnesium, have also been described by Bonsdorff.

BROMATES OF MERCURY. These salts have been examined by Rammeisberg. (*Poggend.*, lv. 79.) *Bromate of the suboxide of mercury* is thrown down in the form of white powder on mixing solutions of bromate of potassa and nitrate of suboxide of mercury: the precipitate becomes yellowish by continued washing, from the formation of a subsalt, but is again immediately whitened by a few drops of nitric acid. This salt is crystallisable out of its solution in aqueous bromic acid in white anhydrous tables $= \text{Hg}_2\text{O}, \text{BrO}_5$. Hot water immediately resolves it into the yellow subsalt $= 2\text{Hg}_2\text{O}, \text{BrO}_5$; the neutral salt remaining dissolved in the excess of acid. It is difficultly soluble in nitric acid: hydrochloric acid dissolves it and forms corrosive sublimate.

Bromate of red oxide of mercury is formed by digesting the recently precipitated hydrate of the red oxide in aqueous bromic acid, or by precipitating pernitate of mercury by bromate of potassa; it is a white crystalline powder $= \text{HgO}, \text{BrO}_5 + 2\text{HO}$; soluble in 650 parts of cold, and 64 of boiling water. When an aqueous solution of bromate of mercury is slightly supersaturated with ammonia, a pale yellow precipitate falls, which explodes violently when heated: it is represented by Rammeisberg as an hydrated compound of nitruet with bromate of mercury; $= \text{Hg}_3\text{N}, \text{HgO}, \text{BrO}_5, 2\text{HO}$.

FLUORIDES OF MERCURY. Hydrofluoric acid occasions no precipitate in solutions of suboxide of mercury, and when the mixture is evaporated, the acid escapes, and leaves the mercurial salt unchanged. When a mixture of calomel and fluoride of sodium is heated, an impure subfluoride of mercury is formed: it is white, and insoluble in water: it cannot be obtained by sublimation from a mixture of the fluoride and mercury. When hydrofluoric acid is poured upon red oxide of mercury, it acquires an orange color, and is dissolved upon the addition of water. The solution furnishes yellow prismatic crystals, which, by the action of hot water, are resolved into a soluble and insoluble compound. (BERZELIUS.)

MERCURY AND NITROGEN. NITRURET OF MERCURY. Hg_3N . This compound, discovered in 1841, by Plantamour, is formed by passing ammonia over oxide of mercury in a glass bulbed or porcelain tube till saturated; it is then heated in an oil-bath to 300° , (between 250° and 285° , BERZELIUS,) and the current of gaseous ammonia continued as long as water is formed: $3\text{HgO} + \text{NH}_3 = \text{Hg}_3\text{N} + 3\text{HO}$. The product is always contaminated by a little metallic mercury, which may be abstracted by cold dilute nitric acid: it may then be washed and dried. If the due temperature and previous saturation of the cold oxide with ammonia be not observed, the principal product is a mixture of mercury and its suboxide. Nitruet of mercury is a brown powder, which explodes when struck with a hammer, or when suddenly heated, or acted on by concentrated sulphuric acid: in these respects it somewhat resembles iodide of nitrogen. (*Ann. der Pharm.*, XL. 115, and *Bibliothèque Universelle*, N.S., xxxii. 339.)

MERCURY AND NITRIC ACID. NITRATES OF MERCURY. There appear to be three nitrates of the suboxide of mercury, (formerly termed *proto-nitrates of mercury*,) namely, a neutral and two basic salts.

1. The *neutral Nitrate of suboxide of Mercury* $= \text{Hg}_2\text{O}, \text{NO}_5$, is formed by digesting excess of mercury in cold dilute nitric acid till *short prismatic crystals* are formed. (If these be left in the solution they gradually give place to larger crystals of a sesqui-salt.) They are entirely soluble in a small quantity of warm water; by a large quantity of water they are resolved into an acid and basic salt: the *acid salt* (*solutio hydrargyri frigide parata*), is at once obtained by dissolving this, or the subnitrates, in dilute nitric acid. When this neutral salt is triturated with chloride of sodium, and water added, it yields a solution which is neutral to test-paper, and pure calomel remains upon the filter. The crystals are $\text{Hg}_2\text{O}, \text{NO}_5, 2\text{HO}$; consisting of

						C. G. Mitscherlich.	
Suboxide of mercury	1	...	208	...	74.29	...	74.78
Nitric acid	1	...	54	...	19.29	...	19.57
Water	2	...	18	...	6.42	...	6.65
<hr/>							
Crystallized neutral nitrate of } suboxide of mercury.	1		280		100.00		100.00

This salt is resolved by heat into red oxide (*Hydrargyri nitric-oxidum*), and nitrous acid. $\text{Hg}_2\text{O}, \text{NO}_5 = 2\text{HgO} + \text{NO}_4$.

2. *Sesquinitrate of suboxide of Mercury*. $3\text{Hg}_2\text{O}, 2\text{NO}_5$. When the first formed crystals of the preceding salt are left in the mother-liquor, they gradually dissolve, and are replaced by large transparent prisms having the formula $3\text{Hg}_2\text{O}, 2\text{NO}_5, 3\text{HO}$. According to Mialhe, (*Journ. de Pharm.*, xxii. 588,) the same salt is obtained by pouring 2 pounds of strong nitric acid upon 2 pounds of mercury in a flat-bottomed flask standing upon a thick iron plate, so as to keep down the temperature: in 24 hours the salt is formed in large crystals: should, however, a tuberculated saline mass be produced, it must be dissolved in the smallest possible quantity of hot water acidulated with nitric acid, and left to evaporate in a stove: in two days large crystals are obtained, which are to be drained on a filter and washed with a little nitric acid. They are soluble without decomposition in a little water; in much water they pass into a yellow

subsalt and a soluble supersalt : triturated with chloride of sodium, they yield a filtrate on the addition of water, which is free from mercury, and leave a greenish residue, which is a mixture of calomel and suboxide: they consist of

						Mitscherlich.
Suboxide of mercury	3	...	624	...	82.22	82.09
Nitric acid.....	2	...	108	...	14.23	14.21
Water	3	...	27	...	3.55	3.70
<hr/>						<hr/>
Crystallized sesquinitrate of } suboxide of mercury.	1		759		100.00	100.00

Kane represents this as a combination of the neutral and bibasic salt: namely= $\text{Hg}_2\text{O},\text{NO}_5,2\text{HO} + 2\text{Hg}_2\text{O},\text{NO}_5,\text{HO}$.

3. *Bibasic nitrate of suboxide of Mercury.* $2\text{Hg}_2\text{O},\text{NO}_5$, is formed by repeatedly washing either of the preceding salts with cold water: it remains as a yellow powder. (If hot water be used, the decomposition is quicker, but some metallic mercury is apt to separate.) This salt sometimes forms small yellow crystals, when a solution of the preceding salts is long left over metallic mercury. By long boiling in water a grey powder, consisting chiefly of metallic mercury, separates, and nitrate of the red oxide is found in solution. (KANE.) It consists of

Suboxide of mercury	2	...	416	...	86.85
Nitric acid.....	1	...	54	...	11.27
Water	1	...	9	...	1.88
<hr/>					
Bibasic nitrate of suboxide of mercury	1		479		100.00

Nitrates of the red oxide of Mercury. Pernitrates of Mercury. 1. There is no crystallizable *monobasic nitrate of red oxide of mercury* = HgO,NO_5 . When peroxide of mercury is dissolved in nitric acid, or when mercury is boiled in strong nitric acid, a dense liquor is obtained on evaporation, (sp. gr. 3.47, PROUST,) which stains the cuticle brown; on further evaporation acid escapes and crystals of *dipernitrate* are formed. So also when corrosive sublimate is decomposed by an atomic equivalent of nitrate of silver a filtrate is obtained which must contain HgO,NO_5 ; but on evaporation it yields the subsalt. The concentrated liquor yields a precipitate of yellow *tribasic* salt by the addition of water, but the acid solution is not precipitated on further dilution.

Preuss and Souville have described crystalline compounds of this nitrate of mercury with iodide of mercury. (*Annalen der Pharm.*, xxix. 326, and *Journ. de Pharm.*, xxvi. 474.)

2. *Bibasic nitrate of red oxide of Mercury. Dipernitrate of Mercury.* $2\text{HgO},\text{NO}_5$. This is the salt which crystallizes out of the preceding solution when it is evaporated: it is deliquescent, decomposed by water, but soluble without change in water acidulated by nitric acid: its crystals are $2\text{HgO},\text{NO}_5,2\text{HO}$, or

						Mitscherlich.
Red oxide of mercury.....	2	...	216	...	75.00	75.88
Nitric acid	1	...	54	...	18.75	18.90
Water	2	...	18	...	6.25	5.22
<hr/>						<hr/>
Crystallized bibasic nitrate } of red oxide of mercury }	1		288		100.00	100.00

3. *Tribasic nitrate of red oxide of Mercury.* $3\text{HgO},\text{NO}_5$, remains in the form of a yellow hydrated powder $= 3\text{HgO},\text{NO}_5,\text{HO}$, when the preceding salt is drenched with cold water as long as it runs off sour: it contains 76 to 78 per cent. of mercury: its proximate components are

Red oxide of mercury	3	324	83.72
Nitric acid.....	1	54	13.95
Water	1	9	2.33
<hr/>					
Tribasic nitrate of red oxide } of mercury.	1		387		100.00

Sexbasic nitrate of red oxide of Mercury. $6\text{HgO},\text{NO}_5$, is formed by the continuous action of boiling water on the yellow tribasic salt: it is a brick-colored powder, which when heated evolves yellow fumes and a trace of water, and leaves red oxide: it contains about 86 per cent. of mercury (KANE), its components being

Red oxide of mercury	6	648	92.31
Nitric acid	1	54	7.69
<hr/>					
Sexbasic nitrate of red oxide } of mercury.	1		702		100.00

Action of ammonia on the nitrates of Mercury. 1. *Ammonio-nitrate of suboxide of Mercury.* *Hahnemann's Soluble Mercury.* $3\text{Hg}_2\text{O}, + \text{NH}_4\text{O},\text{NO}_5$. This compound is obtained by precipitating a very dilute cold aqueous solution of nitrate of suboxide of mercury, as free as possible from excess of acid and from peroxide, by the gradual addition of a weak aqueous solution of ammonia; the mixture should be constantly stirred, the ammonia not added in excess, and the precipitate washed as quickly as possible upon a filter, and dried in the shade at ordinary temperature. (If these precautions are not attended to, other products are obtained.) It is a greyish-black powder, slowly decomposed by the action of light, with the separation of metallic mercury: it is entirely soluble in hot hydrochloric acid, and in acetic acid (with the exception generally of a few globules of mercury.) Gmelin represents its decomposition by boiling in hydrochloric acid as follows: $3\text{Hg}_2\text{O},\text{NH}_4\text{O},\text{NO}_5 + 7\text{HCl}, = 6\text{HgCl} + \text{NH}_4\text{Cl} + \text{NO}_2 + 7\text{HO}$. The proximate components of this compound may be represented as

						Mitscherlich.
Suboxide of mercury	3	624	88.63 88.95
Ammonia.....	1	17	2.42 2.46
Nitric acid	1	54	7.67 7.32
Water	1	9	1.28 1.17
<hr/>						
Ammonio-nitrate of suboxide of mercury	1		704		100.00	100.00

2. *Nitrate of ammonia and of suboxide of Mercury.* By evaporating a mixed solution of nitrate of suboxide of mercury and nitrate of ammonia, Pagenstecher obtained prismatic crystals, the aqueous solution of which gave a grey precipitate both with ammonia and with carbonate of potassa.

3. *Basic amido-nitrates of Mercury.* (a) $\text{HgNH}_2 + 5\text{HgO},\text{NO}_5$. This compound appears to be sometimes formed when excess of ammonia is added to a concentrated nitrate of peroxide of mercury: it is a pale yellow powder containing about 85 per cent. of mercury. (KANE.)

(β) $\text{HgNH}_2 + 3\text{HgO},\text{NO}_5$. This has been distinguished as *Soubeiran's*

ammonio-subnitrate: it is obtained by adding a slight excess of ammonia to a dilute hot solution of the nitrate of the peroxide: it is a white granular powder: when heated it first becomes yellow, then evolves nitrogen, ammonia, and nitrous fumes, and afterwards oxygen and mercury: it evolves no ammonia, nor is it decomposed by boiling solution of potassa.

(γ) $\text{HgNH}_2 + 2\text{HgO}, \text{NO}_5$. This compound falls on the mixture of diluted aqueous solutions of nitrate of mercury and of ammonia: it is a white powder which remains long suspended, and may be dried at 212° without decomposition: it is converted into salt β when boiled in water.

(δ) $\text{Hg NH}_2 + 2\text{Hg O}, \text{NO}_5 + \text{NH}_4 \text{ O}, \text{NO}_5$. When the preceding salt is dissolved in solution of nitrate of ammonia, yellow crystals of the above composition are obtained on evaporation. (KANE.) Mitscherlich represents them as $2\text{Hg O} + \text{NH}_3, \text{NO}_5$. They are easily decomposed by alkaline hydrosulphurets and by hydrochloric acid, but not by other acids: they are very little soluble in nitric acid, and are not acted upon by sulphuric acid, nor by ammonia or potassa.

(ϵ) $\text{HgNH}_2 + 3\text{Hg O}, \text{NO}_5 + 2[\text{NH}_4 \text{ O}, \text{NO}_5] + 2\text{HO}$; or $4\text{HgO} + 3[\text{NH}_4 \text{ O}, \text{NO}_5]$. The solution of the salt γ in a concentrated boiling solution of nitrate of ammonia, and filtered hot, yields on cooling, shining acicular crystals, which afterwards become opaque, and which contain between 58 and 59 *per cent.* of mercury: they are resolved by water into salt γ and nitrate of ammonia. The same salt is also obtained by boiling peroxide of mercury with nitrate of ammonia. (KANE.)

MERCURY AND SULPHUR. SUBSULPHURET OF MERCURY. DISULPHURET OF MERCURY. Hg_2S . When 1 part of mercury is triturated for some time with 3 of sulphur, a black tasteless compound is obtained, which was called in old pharmacy *Ethiops mineral*; it is the *Hydrargyri sulphuretum cum sulphure* of the Pharmacopœia, and is sometimes regarded as a definite sulphuret; but when boiled in solution of potassa, sulphur is taken up, and monosulphuret $= \text{HgS}$, remains, so that it is probably a mixture of sulphur and of the monosulphuret. According to Taddei, an *Ethiops mineral* may be quickly formed by the following process. (*Gior. di Fisica*, iv. 12.) "Put 1 part of sulphuret of potassa with 3 of mercury into a mortar, and triturate with a little water, until the whole forms a homogeneous black paste; then add flowers of sulphur equal in weight to the mercury, and mix the whole: wash with repeated effusions of water, till the alkaline sulphuret is removed, and carefully dry the remaining *Ethiops*."

When sulphuretted hydrogen is passed through a dilute solution of nitrate of suboxide of mercury, or through a mixture of very finely divided calomel and water, or when the mercurial solution is dropped into an aqueous solution of bisulphuret of potassium, a black powder is thrown down, which is a true disulphuret: the latter process furnishes the purest product: it should be washed, and dried over oil of vitriol: when boiled with nitric acid, it is converted into a sulphate of mercury: heated to redness, metallic mercury escapes, and sulphuret sublimes. By long exposure to light it is said to be resolved into mercury and sulphuret. It contains, according to Guibourt (*Ann. Ch. et Ph.*, i.), 100 mercury + 8.2 sulphur, numbers which correspond to

Mercury	2	200	92·6
Sulphur	1	16	7·4
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Disulphuret of mercury	1		216		100·0

PROTOSULPHURET OF MERCURY. MONOSULPHURET OF MERCURY. VERMILION. CINNABAR. HgS . This sulphuret is obtained by the following processes: (1.) 6 parts of mercury are mixed in an iron pot with 1 of sulphur, and made to combine by a moderate heat, and constant stirring: this compound is then transferred to a glass subliming-vessel, (on a small scale, a Florence flask answers perfectly,) and heated to redness in a sand-bath; a quantity of mercury and of sulphur evaporate, and a steel-grey sublimate forms, which is removed, and rubbed or levigated into a very fine powder. If mercury and sulphur be heated together in large quantities, the action is so intense at the moment of their combination as to occasion an explosive ignition; some sulphuretted hydrogen is also evolved. (2.) When solution of corrosive sublimate is decomposed by the prolonged action of excess of sulphuretted hydrogen, or of alkaline sulphurets, the precipitate which falls is sulphuret of mercury; but it is perfectly black until warmed in the sulphuretted liquor, when it gradually reddens. (3.) Kirchoff was the first who pointed out a mode of obtaining vermilion by triturating mercury and sulphur in a solution of potassa: (*Nicholson's Journ.*, 4to. ii.): a black compound is first formed, and the mixture is then heated to 130° , and retained for several hours at about that temperature, when it gradually acquires a brown and then a red tint; when this is sufficiently brilliant the liquid is decanted, and the product washed and dried. (4.) Liebig obtains vermilion by digesting recently prepared *white precipitate* (see page 980) in a solution of sulphuret of ammonium, obtained by saturating hydrosulphuret of ammonia with sulphur: a black sulphuret is first produced, which afterwards acquires the desired red color; its tint is improved by digestion at a gentle heat in a strong solution of potassa. (5.) Several processes have been given purporting to be those adopted by the Chinese, who have been long celebrated for the preparation of a remarkably brilliant cinnabar. (See GMELIN, *Handbuch*, iii. 484; and DUMAS, *Chim. App. aux Arts*, iii. 623.) According to Wehrle, this may be attained by subliming common cinnabar with about 1 *per cent.* of sulphuret of antimony: the dark grey product is then reduced by long trituration to impalpable powder, boiled in solution of sulphuret of potassium, thoroughlyedulcorated, digested in hydrochloric acid, again washed, and lastly carefully dried: this is said to yield an excellent product, of a deep and somewhat crimson tint, without any admixture of orange. The principal points to attend to in procuring this pigment of its most perfect hue, are in the first place the careful selection and cleansing of the first crystalline grey sublimate, so that there may not be the smallest remaining admixture of the black pulverulent amorphous compound; and secondly the perfection of the mechanical operation of pulverisation and elutriation, so as to render the powder as impalpable as possible. (*Edin. Journ. Science*, ii. 352.)

Cinnabar is not altered by exposure to air or moisture; when heated to dull redness in an open vessel, the sulphur forms sulphurous acid, and the mercury escapes in vapor. It is decomposed by distillation with fixed alkalis, lime, and baryta, and by several of the metals. When

adulterated with red-lead or with colcothar, it is not entirely volatile. It is insoluble in caustic alkaline solutions, and in nitric and hydrochloric acid; but nitrohydrochloric acid acts upon, and decomposes it, even in the cold. Boiled in sulphuric acid, sulphurous acid is evolved, and a sulphate of mercury formed. It consists of

						Seftström.	Guibourt.	Seguin.	Proust.				
Mercury	1	...	100	...	86·2	...	86·29	...	86·21	...	85·5	...	85
Sulphur	1	...	16	...	13·8	...	13·71	...	13·79	...	14·5	...	15
<hr/>													
Protosulphuret of mercury }	1		116		100·0		100·00		100·00		100·0		100

Native Cinnabar is the principal ore of mercury: it occurs massive, and crystallized in six-sided prisms, rhombs, and octohedra. It is of various colors, sometimes appearing steel-grey, at others bright-red. It occurs in Hungary, France, and Spain, in Europe; in Siberia and Japan, in Asia; and in considerable quantities in South America. It has also been imported from China. The mines of Almaden, and of New Spain, are the most productive, and furnish fine cabinet specimens. Native mercury, and native amalgam of silver, sometimes accompany it.

CHLOROSULPHURET OF MERCURY. $2\text{HgS}, \text{HgCl}$. When sulphuretted hydrogen gas is passed through a solution of corrosive sublimate a white precipitate is first formed, which is long in subsiding, and readily passes through filtering paper: if the action of the gas be continued, this white compound blackens and becomes sulphuret of mercury. The same white compound is formed by digesting moist and recently precipitated sulphuret of mercury in a solution of corrosive sublimate. It may be washed, and dried without decomposition: when heated, corrosive sublimate rises first, and afterwards sulphuret of mercury: it is insoluble in the greater number of acids, but nitrohydrochloric acid decomposes it. Heated in a stream of chlorine it yields chloride of sulphur and corrosive sublimate: $2\text{HgS}, \text{HgCl} + 3\text{Cl} = 3\text{HgCl} + \text{S}_2 \text{Cl}$. The alkalis blacken it, and forming chlorides of their bases, separate sulphur and oxide of mercury. (ROSE, *Poggend.*, xiii. 59.) Its components are

						H. Rose.	
Mercury	3	...	300	...	81·52	...	81·70
Sulphur	2	...	32	...	8·69	...	8·76
Chlorine	1	...	36	...	9·79	...	9·26
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Chlorosulphuret of mercury	1		368		100·00		99·72

IODOSULPHURET OF MERCURY. $2\text{HgS}, \text{IIgI}$. This is a yellow compound obtained by the action of sulphuretted hydrogen upon iodide of mercury. It is resolved by heat into iodide and sulphuret of mercury.

BROMOSULPHURET OF MERCURY, $2\text{HgS}, \text{HgBr}$, is obtained by the action of sulphuretted hydrogen upon solution of bromide of mercury, the latter being in excess: it is also formed by digesting freshly precipitated sulphuret of mercury in solution of bromide of mercury: it is a pale yellow compound, resolved by heat into bromide and sulphuret of mercury: it is more slowly blackened by the alkalis than the corresponding chlorine compound: it is neither dissolved nor decomposed by boiling nitric or sulphuric acid. (II. ROSE.)

FLUOSULPHURET OF MERCURY. $2\text{HgS}, \text{HgF}$. When a solution of fluoride of mercury in hydrofluoric acid is subjected to the action of sulphuretted hydrogen, a white precipitate is obtained, which is characteristically distinguished from the preceding combinations by its being decomposed by boiling water into sulphuret of mercury and fluoride of mercury. When heated with sulphuric acid, hydrofluoric acid is disengaged. (H. ROSE.)

HYPOSULPHITES OF MERCURY. When a solution of an alkaline hyposulphite is poured into a very dilute solution of nitrate of suboxide of mercury it occasions a black precipitate, which, however, is not a true hyposulphite. With the salts of the peroxide the precipitate is white or yellow, and is, according to Rose, a compound of the mercurial salt with sulphuret of mercury.

When finely-divided peroxide of mercury is dissolved in a warm solution of hyposulphite of ammonia, and alcohol added to the solution, prismatic crystals are formed $= 4 [\text{NH}_4 \text{O}, \text{S}_2 \text{O}_2] + \text{HgO}, \text{S}_2 \text{O}_2, + 2\text{HO}$. When their aqueous solution is boiled, it deposits a black precipitate of sulphuret of mercury, which gradually passes into cinnabar. (RAMMELSBURG, *Poggend.*, lvi. 318.)

SULPHITES OF MERCURY. These salts appear not to exist. When sulphurous acid acts upon oxide of mercury, it forms, according to Berzelius, a sulphate of the suboxide, which, on the further addition of sulphurous acid, is reduced to the metallic state: the same thing, he observes, happens, when any salt of suboxide of mercury is heated with hyposulphite of potassa. A solution, containing only a 100,000th part of nitrate of suboxide of mercury, is rendered brown by the addition of an alkaline hyposulphite, in consequence of the production of sulphuret of mercury.

HYPOSULPHATES OF MERCURY. Freshly precipitated suboxide of mercury dissolves in hyposulphuric acid, and affords, on evaporation, a white crystalline salt containing 74.78 *per cent.* of the oxide; it is therefore neutral and anhydrous: it dissolves difficultly in water, easily in dilute nitric acid, is blackened by boiling with water, decomposed by alkalis, and is resolved at a high temperature into metallic mercury, sulphurous acid, and sulphate of mercury. A neutral salt of the peroxide does not exist; but when excess of peroxide of mercury is digested with hyposulphuric acid, a yellowish-white basic salt is formed, soluble in dilute hydrochloric acid. (RAMMELSBURG, *Poggend.*, lviii. and lix. *Chem. Gaz.*, July, 1843.)

SULPHATE OF SUBOXIDE OF MERCURY. $\text{Hg}_2\text{O}, \text{SO}_3$. When 1 part of mercury is digested in a moderate heat with $1\frac{1}{2}$ of sulphuric acid, sulphurous acid gas is evolved, and a white deliquescent mass is obtained, which, washed with cold water, affords a very difficultly-soluble white salt, which is a *sulphate of suboxide of mercury*. The same salt is thrown down, when sulphuric acid or sulphate of soda is added to a solution of nitrate of suboxide of mercury: it is also formed by triturating equivalent proportions of mercury and persulphate, and heating the mixture, as in the process for making calomel (p. 975). Sulphate of suboxide of mer-

cury requires 500 parts of cold, and 300 of boiling water for its solution: it crystallizes in prisms. According to Fourcroy, it is soluble in dilute sulphuric acid, and thus forms a crystallizable supersalt. It is soluble in dilute nitric acid, from which it is almost entirely precipitated by dilute sulphuric acid. (WACKENRODER.) Its solution in boiling water is decomposed by the fixed alkalis, which at first throw down a basic salt, and when added in excess, separate the black oxide. Its decomposition by chloride of sodium in the production of calomel, has been above described. This salt, when anhydrous, consists of

							Kane.
Suboxide of mercury	1	...	208	...	83·87	...	83·98
Sulphuric acid	1	...	40	...	16·13	...	16·02
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Sulphate of suboxide of mercury	1		248		100·00		100·00

SULPHATE OF PEROXIDE OF MERCURY. PERSULPHATE OF MERCURY. HgO, SO_3 . This salt is formed when 2 parts of mercury and 3 of sulphuric acid are boiled down to dryness: sulphurous acid is evolved during the process (p. 975.) It is also obtained by dissolving 1 atom of oxide of mercury in somewhat more than 1 atom of oil of vitriol, and evaporating to dryness: the oxide should be in fine powder, and the acid diluted with about 3 parts of water; the process is best performed in a platinum crucible, and any excess of acid may be expelled by raising the heat nearly to redness, for the salt bears that temperature without decomposition; at a dull red-heat it becomes orange-colored, but again white on cooling, and at a somewhat higher temperature it evolves oxygen and sulphurous acid, mercury distils over, and a little of the sulphate of the suboxide sublimes. Berzelius observes that if this operation be suspended, the residue is always undecomposed sulphate, so that its decomposition only ensues at the moment of its volatilization. When dry hydrochloric gas is conducted over this salt at common temperatures, it has no effect upon it; but if it be heated at any one point, decomposition begins there, and continues through the whole mass, so as to convert the whole into a mixture of chloride of mercury, sulphuric acid, and water; $\text{HgO}, \text{SO}_3, + \text{HCl} = \text{HgCl} + \text{SO}_3, \text{HO}$; and as the corrosive sublimate is more volatile than the oil of vitriol, they may be separated by the due application of heat. Similar decomposition ensues with hydriodic and hydrocyanic acid. This sulphate of mercury is decomposed in the humid way by all the hydracids, and free sulphuric acid is found in solution. Its decomposition by chloride of sodium in the production of corrosive sublimate has already been noticed. It is resolved by water into a soluble acid salt and an insoluble basic salt: the former may be obtained in white deliquescent acicular crystals, which have not been specially examined. This sulphate consists of

							Kane.
Peroxide of mercury	1	...	108	...	72·97	...	72·98
Sulphuric acid	1	...	40	...	27·03	...	27·02
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Sulphate of peroxide of mercury } (persulphate of mercury) }	1		148		100·00		100·00

TRIBASIC SULPHATE OF PEROXIDE OF MERCURY. SUBPERSULPHATE OF MERCURY. $3\text{HgO}, \text{SO}_3$. This salt (long known under the name of

Turpeth mineral, from a similarity in its medical effects to those of the root of the *Convolvulus Turpethum*, which is violently cathartic and emetic,) is obtained in the form of an almost insoluble yellow powder by the action of boiling water upon the preceding sulphate: it is also precipitated upon the mixture of boiling solutions of pernitrate of mercury and sulphate of soda: its specific gravity is 6·4; it requires about 2000 parts of cold, and 600 of boiling water for solution: when gently heated, its color gradually deepens to orange, but reverts to lemon-yellow as it cools. It consists of

						Kane.	R. Phillips.
Peroxide of mercury	3	...	324	...	89·01	...	88·90
Sulphuric acid.....	1	...	40	...	10·99	...	10·95
<hr/>							
Tribasic sulphate of peroxide of mercury }	1		364		100·00		99·85
							100·0

Action of ammonia on the sulphates of mercury. (a.) *Tribasic amido-sulphate of suboxide of mercury.* $3\text{Hg}_2\text{O},\text{SO}_3 + \text{Hg}_2\text{NH}_2$. This compound is the result of the action of aqueous ammonia upon sulphate of suboxide of mercury; it is a dark-grey powder which is resolved by heat into water, ammonia, sulphurous acid, oxygen, and mercury. Kane represents it as constituted of

Mercury	2	...	200	...	22·73
Amidogen	1	...	16	...	1·82
Suboxide of mercury ...	3	...	624	...	70·91
Sulphuric acid	1	...	40	...	4·54
<hr/>					
$\text{Hg}_2\text{NH}_2 + 3\text{Hg}_2\text{O} + \text{SO}_3$	1		880		100·00

(β.) *Tribasic amido-sulphate of peroxide of mercury.* $\text{HgNH}_2 + 3\text{HgO},\text{SO}_3$. This compound, which is represented by Rammelsberg (*Poggend.*, LV. 85) as containing nitruet of mercury, sulphate of mercury, and water [$\text{Hg}_3\text{N} + \text{HgO},\text{SO}_3 + 2\text{HO}$], is obtained by the action of solution of ammonia on persulphate of mercury: it has sometimes been called *ammoniacal turpeth*, inasmuch as it is also formed when that tribasic subsalt is digested in a solution of sulphate of ammonia till it is converted into a white powder, an ammonio-sulphate of peroxide of mercury being at the same time formed: $2[3\text{HgO} + \text{SO}_3] + 3[\text{NH}_4\text{O},\text{SO}_3] = [\text{HgNH}_2 + 3\text{HgO},\text{SO}_3] + 2[\text{NH}_4\text{O},\text{SO}_3 + \text{HgO},\text{SO}_3] + 2\text{HO}$. It is a heavy white powder, which becomes brown when heated; when diffused in water and subjected to the action of sulphuretted hydrogen, it yields sulphuret of mercury and a neutral solution of sulphate of ammonia. (KANE.) Its components are represented as

						Kane.
Mercury.....	4	...	400	...	83·34	...
Amidogen	1	...	16	...	3·33	...
Oxygen	3	...	24	...	5·00	...
Sulphuric acid	1	...	40	...	8·33	...
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$\text{HgNH}_2 + 3\text{HgO} + \text{SO}_3$	1		480		100·30	

(γ.) *Ammonio-sulphate of peroxide of mercury.* $\text{NH}_4\text{O},\text{SO}_3 + \text{HgO},\text{SO}_3$. This is a difficultly soluble salt, which falls in the form of a white powder on mixing solutions of the component sulphates: it is soluble in excess of ammonia. (FOURCROY, *Ann. de Chim.*, xiv. 34.)

PHOSPHURET OF MERCURY may be formed by heating phosphorus with oxide of mercury, or with the subsulphuret (PELLETIER); or by passing the vapor of phosphorus over calomel (DAVY); or phosphuretted hydrogen through a solution of nitrate of suboxide of mercury (THOMSON); or by passing phosphuretted hydrogen through dry and gently heated corrosive sublimate, when phosphuret of mercury sublimes. (H. ROSE, *Poggend.*, xxiv. 335.) It varies in appearance, and according to the method of its production its color is either brown or black: prepared by Rose's process, it forms a brown or orange-colored sublimate, which, when suddenly heated, is resolved into phosphorus and mercury. When obtained by the action of phosphuretted hydrogen upon mercurial solutions, it almost always contains portions of the salt employed; and by acting upon solutions of persalts of mercury by phosphuretted hydrogen, the first precipitate is white or yellow, and is a compound of phosphuret of mercury and the salt of the oxide. These combinations have been described by H. Rose. (*Ann. Ch. et Ph.*, Lxvi. 366.)

HYPOPHOSPHITE and PHOSPHITE OF MERCURY cannot be formed, as those acids reduce the oxides and salts of mercury.

PHOSPHATES OF MERCURY. (*α.*) When solution of common phosphate of soda is dropped into a solution of suboxide of mercury, a white crystalline precipitate falls, which is a *bibasic phosphate of suboxide of mercury* $= 2\text{Hg}_2\text{O}, \text{PO}_5$ [$2\text{Hg}_2\text{O}, \text{HO} + c\text{PO}_5?$] It is insoluble in water and in excess of phosphoric acid, and when heated, leaves a yellow vitreous phosphate of the peroxide. (DULONG, *Mem. d'Arcueil.*) When boiled with water it is converted into a grey powder, which is a mixture of mercury with undecomposed salt, and phosphate of the peroxide is found in solution. (H. ROSE.) It is blackened by boiling hydrochloric acid in consequence of separated mercury and formation of perphosphate. It is entirely decomposed by solution of potassa, and the whole of the mercury precipitated. It consists, when thoroughly dried at 212° , of

						Trommsdorff.	
Suboxide of mercury	2	416	85.25	85.9
Phosphoric acid	1	72	14.75	14.4
<hr/>						<hr/>	
Bibasic phosphate of suboxide of mercury	1		488		100.00		100.0

(*β.*) *Pyrophosphate of Suboxide of Mercury.* When a mixture of crystallized nitrate of suboxide of mercury and pyrophosphate of soda is triturated with cold water, a black precipitate falls, and the liquid contains a salt of the suboxide, free from protoxide: with boiling water, the precipitate is blacker, and a mixture of the phosphate of the suboxide and of the oxide is found in solution. (H. ROSE.) According to Gmelin, pyrophosphate of soda occasions a white precipitate in solution of nitrate of suboxide of mercury, neither soluble in nor discolored by excess of the soda salt. (*Handbuch.*)

(*γ.*) *Phosphate of peroxide of Mercury.* $2\text{HgO}, \text{PO}_5$. *Perphosphate of Mercury.* This salt falls in the form of a dense white insoluble powder ($= 2\text{HgO}, \text{HO} + c\text{PO}_5?$) on mixing solutions of the nitrate of the peroxide and phosphate of soda; solution of potassa abstracts the whole of its acid, and throws down oxide of mercury: aqueous phosphorous and

sulphurous acid slowly effect a partial reduction of the mercuric oxide: it is soluble in hydrochloric acid, and on evaporating the solution, alcohol abstracts corrosive sublimate from the residue: it is also soluble in solution of sal-ammoniac. Its components, when dried at 212°, are

						Trommsdorff.
Oxide of mercury	2	216	75 75·2
Phosphoric acid	1	72	25 24·8
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Perphosphate of mercury	1		288		100	100·0

SELENIURET OF MERCURY, obtained by heating the metal with selenium, is a tin-colored substance, which sublimes in shining scales at a temperature below its point of fusion; with excess of selenium a grey crystalline mass is obtained.
Native Seleniuret of Mercury has been found in combination with seleniuret of lead.

SELENITE OF SUBOXIDE OF MERCURY, Hg_2O, SeO_2 , is a white, insoluble powder, fusible and volatile at a high temperature. (BERZELIUS.)

SELENITE OF OXIDE OF MERCURY, HgO, SeO_2 , is a white, difficultly soluble powder: dissolved in selenious acid it forms a crystallizable *biselenite* in striated prisms, which fuse in their water of crystallization and sublime when highly heated. (BERZELIUS.)

CARBONATES OF MERCURY. *Carbonate of Suboxide of Mercury*, Hg_2O, CO_2 , is thrown down when solution of carbonate of potassa or soda is dropped into solution of nitrate of suboxide of mercury, in the form of a yellow powder. To obtain a perfect carbonate, Setterberg mixes the nitrate of the suboxide with slight excess of bicarbonate of potassa, and frequently stirs the mixture during several days till all the basic subsalt of mercury is decomposed; he then quickly washes and dries the precipitate in vacuo over oil of vitriol: it then consists of

						Setterberg.
Suboxide of mercury	1	208	90·44 90·79
Carbonic acid	1	22	9·56 9·21
<hr/>						
Carbonate of suboxide of mercury	1		230		100·00	106·00

Carbonate of peroxide of Mercury. Percarbonate of Mercury. $4HgO, CO_2$. Solution of nitrate of mercury affords a reddish-brown precipitate with carbonate of potassa or soda, which is slightly soluble in excess of the alkaline solution, and in aqueous carbonic acid. It dissolves in solution of sal-ammoniac. With solution of corrosive sublimate the above alkaline carbonates throw down oxichloride of mercury. The above precipitate is a basic salt. (R. PHILLIPS, *Ann. Phil.*, xxvi. 109. SETTERBERG, *Poggend.*, xix. 60.) It consists of

						Setterberg.	R. Phillips.
Oxide of mercury	4	432	95·16 94·42 96·1
Carbonic acid	1	22	4·84 4·78 4·4
<hr/>							
Basic carbonate of peroxide of mercury }	1		454		100·00	99·20	100·5

MERCURY AND CYANOGEN. CYANIDE OF MERCURY. $HgCy$. There

are several processes in common use for the preparation of this compound. (1.) By boiling 1 part of finely-powdered peroxide of mercury with 2 of pure Prussian blue in 8 parts of water, a solution is obtained, which if filtered while hot, deposits, on cooling, crystals of the cyanide. (2.) When peroxide of mercury is brought into the contact of the vapor of hydrocyanic acid they act intensely upon each other, and water and cyanide of mercury are immediately formed. The attraction of mercury for cyanogen is so strong, that peroxide of mercury decomposes nearly all the metallic cyanides, not excepting that of potassium; but the salts of palladium decompose cyanide of mercury. (3.) Peroxide of mercury may be digested in aqueous hydrocyanic acid; the oxide, in very fine powder, may be agitated and left in contact with the acid till its odor is lost; more of the acid is then added to the decanted liquid, and on evaporation the cyanide is obtained. Winkler directs this process as follows: 15 parts of ferrocyanide of potassium, 13 of sulphuric acid, and 100 of water, are distilled by a moderate heat nearly to dryness, the vapor being condensed into 30 parts of water; a portion of the resulting acid is put aside, and the remainder mixed with 16 parts of finely-powdered peroxide of mercury, and agitated till the odor of the acid disappears: the solution is then poured off from the undissolved oxide, and the reserved portion of the acid added to it; this is done to saturate a portion of oxide of mercury which the cyanide dissolves in excess: 12 parts of cyanide of mercury are then obtained by evaporation. (4.) To a solution of 2 parts of ferrocyanide of potassium in 15 of boiling water, add 3 parts of dry persulphate of mercury; boil for 15 minutes, and filter off the clear liquid whilst hot: as it cools, cyanide of mercury crystallizes, which must be purified by a second crystallization: evaporate the mother-liquid to dryness and digest the residue in alcohol, which takes up a further quantity of cyanide. In this process there is a mutual decomposition of cyanide of potassium (of the ferrocyanide) and of persulphate of mercury, into cyanide of mercury and sulphate of potassa; cyanide of iron is at the same time precipitated. (LIEBIG.)

Cyanide of mercury forms anhydrous prismatic crystals, their primary form being a right square prism, (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 42,) nearly colorless, or of a pale buff color, at first transparent, permanent in the air, poisonous, and of a nauseous metallic taste: they dissolve in 8 parts of water at 60°, but in less boiling water, and are sparingly soluble in alcohol.

This salt is decomposed by heat, as in the process for obtaining cyanogen, and a brown or black matter remains in the retort, which, according to Johnston, is *paracyanogen* (p. 505.) If distilled with hydrochloric acid, hydrocyanic acid and chloride of mercury are formed: it also is decomposed by hydriodic acid and by sulphuretted hydrogen, an iodide and a sulphuret of mercury, and hydrocyanic acid, being formed. Nitric acid dissolves it without decomposition. It is decomposed when heated with sulphuric acid. The alkalis do not act upon this cyanide. It slowly absorbs a small portion of ammoniacal gas. It consists of

						Gay Lussac.	Porret.
Mercury.....	1	100	79·37 79·91 79·08
Cyanogen	1	26	20·63 20·09	
<hr/>			<hr/>		<hr/>	<hr/>	
Cyanide of mercury	1		126		100·00	100·00	

OXICYANIDE OF MERCURY. When a solution of cyanide is boiled with excess of peroxide of mercury, a compound is obtained in acicular crystals, on evaporation, which is more soluble than the cyanide, and has an alkaline reaction on vegetable colors. The formation of this and the succeeding compound must, as already stated, be avoided in preparing cyanide of mercury. This salt is a tribasic cyanide of peroxide of mercury, $= \text{HgCy}, 3\text{HgO}$. (KUHN.) When strong aqueous hydrocyanic acid is agitated with excess of peroxide of mercury, a white salt is formed, which may be separated by boiling water, and which crystallizes on cooling in transparent four-sided acicular prisms. When gently heated, it blackens and explodes: it is a compound of 1 atom of cyanide with 1 of peroxide of mercury. (JOHNSTON, *Phil. Trans.*, 1839.)

HYDRARGO-CYANIDES. These compounds are formed by digesting cyanide of mercury in solutions of cyanide of potassium, sodium, calcium, barium, &c. *The hydrargo-cyanide of potassium* yields octohedral crystals $= \text{KCy}, \text{HgCy}$.

Cyanide of mercury also forms compounds with chlorides, iodides, bromides, and with several oxisalts. When cyanide of mercury and iodide of potassium are mixed in solution, pearly crystals fall, which, when redissolved, yield large thin brilliant plates, requiring 16 parts of water at 60° for their solution. They are decomposed by heat, and leave a residue of iodide of potassium and charcoal. (*Ann. Ch. et Ph.*, xix. 220.)

FULMINATING MERCURY. FULMINE OF MERCURY. $2\text{Hg}_2\text{O}, \text{Cy}_2\text{O}_2$. This compound was discovered by Mr. Howard. (*Phil. Trans.*, 1800, p. 214.) It is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid, aided by heat. This solution is to be poured, when cool, into two measured ounces of alcohol in a porcelain basin, and gently warmed: it soon begins to effervesce and evolve ethereal vapor, and if the action is too violent, it must be quelled by cooling the vessel, or by the addition of a little cold alcohol. During this action a yellow-grey precipitate falls, which is to be immediately separated by decantation and filtration, washed with small quantities of distilled water, and carefully dried at a heat not exceeding 100° . The above quantity of mercury yields about 120 grains of the powder, when the operation has been most successful. If the product is mixed with metallic mercury, it may be purified by solution in boiling water, from which it is deposited in silky acicular crystals.

This dangerous compound is now in considerable demand for the manufacture of percussion caps: according to Cremascoli, the following is the safest mode of preparing it: 6 ounces of nitric acid of 1.3 sp. gr. are poured upon half an ounce of mercury in a flask, and held for about a minute in boiling water: as soon as the metal is dissolved, and the temperature of the liquor about 55° , it is poured into and mixed with 4 ounces of alcohol, sp. gr. 0.833; the flask is then again immersed for 2 or 3 minutes in boiling water, or till dense white vapor rises; it is then removed to a cool place; very moderate action ensues, and in the course of some hours the fulminating mercury is deposited in the form of a crystalline precipitate, which, when washed and dried, weighs 5 drachms. It is introduced into the percussion caps, moistened with a little tincture of benzoin, so as

to be dropped in, and subsequently carefully dried; it is also sometimes mixed with about 6 *per cent.* of powdered nitre and a little water, and this dropped into the cap also adheres when dry. The greatest caution is always required in preparing and dealing with fulminating mercury, for it not only sometimes explodes with trifling friction, but may do so in a moist state; and even in the most careful and skilful hands, it cannot be meddled with without considerable danger, a melancholy proof of which was furnished by the lamentable death of Mr. Hennell, at Apothecaries' Hall, on the 4th of June, 1842; he was in the act of mixing two separate portions of the powder in a moist state, with an ivory knife, when the whole quantity, amounting to above 6 lbs., exploded, and shattered his head, breast, and right arm to atoms: a man standing within four yards of him was not injured, but the windows of the immediately surrounding buildings were broken, and a large wooden block, upon which one of the basins was placed, was shivered, as was also the pavement upon which it stood.

This compound, when heated to about 300° , (367° BERZELIUS,) explodes with a bright flame: it also detonates by friction, by the electric spark, and by contact of concentrated sulphuric and nitric acids: the gases evolved by its explosion are carbonic acid, nitrogen, and the vapor of mercury. Liebig and Gay Lussac have furnished some curious facts towards the history of this compound. (*Ann. Ch. et Ph.*, xxiv. and xxv.) Howard endeavoured to substitute it for gunpowder, but the explosion is so sudden as to burst the gun without expelling the shot. It consists of

Suboxide of mercury	2	...	416	...	86.0		2	...	416	...	86
Cyanogen.....	2	...	52	...	10.7	} Fulminic acid }	1	...	58	...	14
Oxygen	2	...	16	...	3.3						
<hr/>											
Fulminate of mercury	1		484		100.0		1		484		100

FERROCYANIDE OF MERCURY. When any solution of a mercurial salt is mixed with ferrocyanide of potassium, a white precipitate falls, which decomposes spontaneously into cyanide of iron, and cyanide of mercury; the latter is dissolved, and if a salt of the suboxide has been used, metallic mercury is also separated: these changes are accelerated by heat.

SULPHOCYANIDE OF MERCURY. When sulphocyanide of potassium is mixed with nitrate of suboxide of mercury, a white precipitate falls. See Wöhler (*Gilb. Annalen*, Lxix.), and Berzelius (*Lehrbuch*), in reference to these compounds, under the head of *Rhodanides of mercury*.

BORATES OF MERCURY. When solution of nitrate of suboxide of mercury and of borate of soda are mixed and evaporated, small shining crystals are obtained, which, according to Berzelius, consist of basic nitrate of mercury, while the boracic acid, in the form of a supersalt, remains in solution. A compound of boracic acid and oxide of mercury may be formed by careful fusion, but it is decomposed by boiling water.

ARSENITES OF MERCURY. Aqueous arsenious acid, and arsenite of potassa, give a white precipitate with nitrate of protoxide of mercury, which is soluble in nitric acid: the same salt is formed by digesting mer-

cury in aqueous arsenic acid. (BERZELIUS.) The precipitate formed by arsenious acid in nitrate of peroxide of mercury is white, soluble in nitric acid, and soluble also in excess of arsenite of potassa.

ARSENIATES OF MERCURY. *Bibasic arseniate of suboxide of mercury*, $2\text{Hg}_2\text{O}, \text{AsO}_5$, falls in the form of a white precipitate, which reddens on drying, when nitrate of suboxide of mercury is dropped into concentrated aqueous solution of arsenic acid. If the solution of arsenic acid, or of arseniate of soda, be dropped into the mercurous solution, a white *arsenio-nitrate* falls, which, especially when heated, becomes yellow, orange-colored, and red or purple, assuming the color of the pure arseniate of the suboxide. This precipitate sometimes forms fine acicular crystals, which lose water of crystallization when heated above 212° , and at higher temperatures are resolved into mercury and arseniate of mercury, and ultimately into mercury, arsenious acid, and oxygen. It is soluble without decomposition in cold nitric acid, and precipitable from it by ammonia; by boiling nitric acid it is converted into perarsenate: it is insoluble in water, in acetic acid, and in alcohol. (SIMON, *Poggend.*, xLi. 424.) The crystallized salt is $2\text{Hg}_2\text{O}, \text{AsO}_5, 2\text{HO}$. The anhydrous salt consists of

						Simon.	
Suboxide of mercury	2	...	416	...	78.34	...	80.1
Arsenic acid	1	...	115	...	21.66	...	19.9
<hr/>							
Bibasic arseniate of suboxide of mercury	1		531		100.00		100.0

Monobasic arseniate of suboxide of mercury, $\text{Hg}_2\text{O}, \text{AsO}_5$, is obtained by evaporating a solution of the preceding salt (or of suboxide of mercury) in aqueous arsenic acid, to dryness, triturating the white residue with water, washing, and drying the remaining white powder in a water-bath: it is insoluble in water, in alcohol, and in acetic acid: its components are

						Simon.	
Suboxide of mercury	1	...	208	...	64.4	...	62.66
Arsenic acid.....	1	...	115	...	35.6	...	37.34
<hr/>							
Monobasic arseniate of suboxide of mercury	1		323		100.0		100.00

Arseniate of peroxide of Mercury. Perarsenate of Mercury. Arsenic acid occasions a white precipitate in solution of nitrate of peroxide of mercury, and arseniate of soda forms a yellow precipitate in solution of corrosive sublimate. (BERGMAN.)

MOLYBDATE OF MERCURY. Molybdic acid occasions a yellow precipitate in solutions of suboxide of mercury, easily soluble in nitric acid. Molybdate of potassa also throws down a yellow precipitate from the nitrate, which is very sparingly soluble in water, and decomposed by nitric acid. (HATCHETT.) Berzelius has described several compounds of sulphurets of molybdenum and sulphurets of mercury. (*Lehrbuch*, and *Poggend.*, vii. 277.)

CHROMATE OF MERCURY. Chromate of potassa throws down an orange-red precipitate from the solution of nitrate of suboxide of mercury: its color is brightest when the solution is acid, but in that case a portion of chromate remains dissolved. This salt is an excellent source

of oxide of chromium, which remains when it is heated so as to expel mercury and oxygen: it is sparingly soluble in water, in nitric acid, and in solution of sal-ammoniac and of nitrate of ammonia: its composition is represented by Gmelin as $4\text{Hg}_2\text{O}, 3\text{CrO}_3$; it contains about 80 *per cent.* of mercury, and 12 of chromic acid. Chromate of potassa added to solution of pernitrate of mercury or of corrosive sublimate gives a precipitate of the same color as the preceding, and the liquor holds bichromate of potassa in solution. (GMELIN.)

VANADIATES OF MERCURY. Vanadate of ammonia forms yellow precipitates in the nitrates of both of the oxides of mercury. (BERZELIUS.)

TUNGSTATES OF MERCURY. Tungstate of soda gives a yellow precipitate in solution of nitrate of suboxide of mercury, containing about 67 *per cent.* of oxide and 37 of acid, and being therefore $\text{Hg}_2\text{O}, \text{WO}_3$. With solution of corrosive sublimate the precipitate is white and insoluble in water: it contains about 57 *per cent.* of oxide of mercury, and 43 of tungstic acid, and is $3\text{HgO}, 2\text{WO}_3$: if pernitrate of mercury, as neutral as possible, be precipitated by tungstate of soda, the white insoluble powder which falls contains 38 *per cent.* of oxide and 62 of acid, and is $2\text{HgO}, 3\text{WO}_3$. (ANTHON, *Buchners Repertorium*, LXXVI. 349.)

ALLOYS OF MERCURY. AMALGAMS. Mercury combines with most of the other metals, and forms a class of compounds generally called *amalgams*. Many of these are definite and crystallizable compounds, and may be separated, by gentle pressure, from the mercury in which such definite compound is suspended or dissolved. They are generally brittle or soft. The extraordinary phenomena connected with the amalgam of *ammonium*, and the probable nature of that substance, have already been discussed. (See page 358.) 1 part of *potassium* with 70 of mercury produce a hard brittle compound. If mercury be added to the liquid alloy of *potassium* and *sodium*, an instant solidification ensues, and heat enough to inflame the latter metals is evolved. *Iron* and mercury may be combined by triturating together clean iron filings and zinc-amalgam, and adding a solution of perchloride of iron: by rubbing and heating this mixture, the iron and mercury form a bright amalgam. (ARTHUR AIKIN.) Under common circumstances, iron resists the action of mercury so perfectly, that the latter metal is usually kept in iron bottles; and mercurial troughs and barometer cisterns are made of the same metal. The use of an amalgam of *zinc* has already been adverted to for the excitation of electrical machines. 8 parts of mercury and 1 of zinc form a white brittle compound: 5 of mercury and 2 of zinc form a crystallizable amalgam. Amalgam of *tin* is easily formed by triturating the metals together, or by fusion at a gentle heat: its density exceeds the mean of its components: it is largely used for silvering looking-glasses. This beautiful process is performed as follows:—A single and perfect sheet of tin-foil, of proper thickness, and somewhat larger than the plate of glass, is spread upon a perfectly plane table of slate or stone: mercury is then poured upon it, and rubbed upon its surface by a hare's foot, or a ball of flannel or cotton, so as to form a clean and bright amalgam; upon this, excess of mercury is poured, till the metal has a tendency to run off: the plate of glass, previously

made quite clean, is then brought horizontally towards the table, and its edge so adjusted, as by gradually and steadily sliding it forward, to displace some of the excess of mercury, and float the plate as it were over the amalgam, the dross upon its surface being pushed onwards by the edge of the glass, so that the mercury appears beneath it with a perfectly uniform, clean, and brilliant reflecting surface: a number of square iron weights, of 10 or 12 lbs. each, are now placed side by side upon the surface of the plate, so as entirely to cover it, and press it down upon the amalgamated surface of the tin; in this way the excess of mercury is partly squeezed out, and the amalgam is made to adhere firmly to the glass. The mercury, as it runs off, is received into a channel on the side of the table, which is slightly inclined to facilitate the drainage, and in about 48 hours the weights are taken off and the plate is carefully lifted from the table and set nearly upright, by which the adhering mercury gradually drains off, and the solid crystalline amalgam remains, perfectly and uniformly adhering to the glass. *Cadmium* and mercury unite with great ease, and the amalgam crystallizes in octohedra, when composed of 100 mercury + 28 cadmium (an atom of each metal); it fuses at 167° . (STROMEYER.) The amalgam of *cobalt* was obtained by Böttger as the result of the action of sodium amalgam upon a saturated solution of chloride of cobalt; it was less fluid than mercury, and admitted of the expulsion of a portion of the latter metal by heat. Damour procured this amalgam of cobalt by the action of an amalgam of 1 part of zinc and 6 of mercury upon chloride of cobalt supersaturated by ammonia; he abstracted the excess of zinc by boiling dilute sulphuric acid, which does not act upon the cobalt amalgam: the mercury may be driven off by heat, and the cobalt remains in the form of a grey magnetic residue. (*Journ. Prakt. Chem.*, xvii. 346.) Amalgam of *nickel* is obtained by processes similar to those applied to cobalt; it is solid, magnetic, and by exposure to air the nickel gradually oxidizes so as to leave fluid mercury. (DAMOUR.) Amalgam of *copper* may be made as follows:—To a hot solution of sulphate of copper add a little hydrochloric acid and a few sticks of zinc, and boil the mixture for about a minute; by this means the copper will be precipitated in a metallic state, and in a finely-divided spongy form: take out the zinc, pour off the liquor, wash the copper with hot water, and pour upon it a little dilute nitrate of mercury, which will instantly cover every particle of copper with a coating of mercury: then add mercury to the amount of two or three times the weight of the copper, and a slight trituration will combine them so far that the completion of the process may be effected by heating the mixture for a few minutes in a crucible. (AIKIN'S *Dictionary*, Art. MERCURY.) *Lead* and mercury readily combine in all proportions: 3 parts of mercury and 2 of lead form a crystallizable amalgam. *Antimony* amalgamates difficultly, and forms a granular compound. *Bismuth* and mercury readily unite: 2 parts of mercury poured into 1 of melted bismuth form a compound which slowly solidifies and crystallizes. When mercury is combined with a little bismuth, lead may be added without greatly interfering with the fluidity of the compound. Dr. Thomson states that Beccher was the first who observed the remarkable fluidity of a mixture of 3 parts of mercury, 1 of lead, and 1 of bismuth, and that it may be squeezed through leather without decomposition: it is used for silvering the inside of hollow glass spheres, which are previously made perfectly

clean and warm. When mercury is adulterated, it is with these metals; but the facility with which it then oxidizes, and the imperfect fluidity of its small globules, render the fraud easy of detection. The action of mercury on the other metals which have been described has not been examined, with the exception of that on *tellurium* and *arsenic*. With tellurium, it forms a granular compound: with arsenic, a grey amalgam of 5 parts of mercury and 1 of arsenic: the metals require to be stirred together for some hours over the fire. Dumas suggests the examination of the action of arsenuretted hydrogen on the chlorides of mercury.

CHARACTERS OF THE SALTS OF MERCURY. The soluble salts of the *suboxide* are mostly white, and of a metallic and nauseous taste: some of them, when neutral, are resolved by water into basic and acid salts: with phosphorous and sulphurous acids, and protochloride of tin, they give precipitates of metallic mercury: the caustic alkalis throw down a black powder; the carbonated alkalis, yellow or brown; the alkaline phosphates, white, even in very dilute solutions; sulphuretted hydrogen and the hydrosulphurets, black; hydriodic acid and the iodides, dingy green or yellow; hydrochloric acid and the chlorides, white and curdy; the alkaline chromates, red; ferrocyanide of potassium, white; the oxalates, white, even when very dilute; tincture of galls, brownish-yellow. The soluble salts of the red or *peroxide* of mercury are mostly white when neutral, yellow when basic; they are poisonous, and nauseously metallic to the taste, and are often resolved by water into acid and basic salts: ammonia and carbonate of ammonia produce white precipitates in their solutions; iodide of potassium a red, and infusion of galls, an orange precipitate. Unless in concentrated solution they are not affected by hydrochloric or oxalic acids. Metallic mercury is precipitated from all its solutions by a plate of clean copper. The presence of organic substances interferes considerably with the appearances produced by some of the above tests; hence, in cases of poisoning by corrosive sublimate, peculiar precautions are sometimes required, and in all cases the precipitate should be collected and heated in a tube with a little white flux, or some such reducing agent, so as to separate metallic mercury, the microscopic globules of which are easily sublimed and discerned. (See CHRISTISON on *Poisons*; TAYLOR'S *Medical Jurisprudence*; and ROSE'S *Analytical Chemistry*.) The insoluble mercurial salts are mostly volatilized at a red-heat, and they are all decomposed, with the production of metallic mercury, when mixed with a little carbonaceous matter, and heated in a glass tube. It appears from the experiments of Mialhe, (*Ann. Ch. et Ph.*, 3 Ser. v. 169,) that all the mercurial preparations used in medicine are, to a greater or less extent, convertible into corrosive sublimate under the influence of the chlorides of the alkaline bases, and he refers the medical effects of mercurials to the formation of corrosive sublimate in consequence of the presence of common salt in the blood and secretions.

§ XXXI. SILVER. Ag. 108.

THIS metal, the *Luna* or *Diana* of the alchemists (D), was known at a very remote period; it is mentioned in the book of Job: it is found

native, and in a variety of combinations; the most common of which is the *sulphuret*.

Native Silver has the general characters of the pure metal. It occurs in masses; arborescent; capillary; and, sometimes, crystallized in cubes and octohedra. It is seldom pure, but contains small portions of other metals, which affect its color and ductility. It is chiefly found in primitive countries. In Peru and Mexico are the richest known mines of native silver. The mines of Saxony, Bohemia, and Swabia, and those of Kongsberg in Norway, are the richest in Europe. It has been found in Cornwall and Devonshire.

Pure Silver may be procured by dissolving the standard silver of commerce in pure nitric acid, diluted with an equal measure of water. Immerse a plate of clean copper into the solution, which soon occasions a precipitate of metallic silver; collect it upon a filter; wash it with solution of ammonia, and then with water, and fuse it into a button.

It may also be procured by adding to the above solution of standard silver, a solution of common salt; collect, wash, and dry the precipitate, and gradually add it to twice its weight of fused carbonate of potassa in a red-hot crucible. Metallic silver is separated, and may be fused into a button.

Silver is of a more pure white than any other metal; it has considerable brilliancy, and takes a high polish. Its specific gravity varies between 10·4, which is the density of cast silver, and 10·5 to 10·6, which is the density of rolled or stamped silver. The specific heat of pure silver is 0·05701. (REGNAULT.) It is so malleable and ductile, that it may be extended into leaves not exceeding a ten-thousandth of an inch in thickness, and drawn into wire infinitely finer than a human hair. Silver melts at a bright red-heat, estimated by Daniell at 1873° of Fahrenheit's scale, and when in fusion appears extremely brilliant. It resists the action of air at high temperatures for a long time, and does not oxidize; the *tarnish* of silver is occasioned by sulphuretted hydrogen; it takes place very slowly upon the pure metal, but more rapidly upon the alloy with copper used for plate, and was found by Proust to be sulphuret of silver. Pure water has no effect upon the metal; but if the water contain vegetable or animal matter, it often slightly blackens its surface, generally in consequence of the presence of sulphur. If an electric discharge be passed through fine silver-wire, it burns into black powder, which is probably an oxide of silver. In the Voltaic circle it burns with a fine green light, and throws off abundant fumes. Exposed to an intense white-heat in the open fire, it boils and evaporates, but in close vessels it is not sensibly volatile. If suddenly cooled, it crystallizes during congelation, often shooting out like a cauliflower, and *spirting* or throwing small particles of the metal out of the crucible. This arises, according to Lucas, from the sudden escape of oxygen, which the metal absorbs and retains whilst fluid, but suddenly gives it off when it solidifies: this property of absorbing oxygen is prevented by the presence of a quantity of copper, not exceeding 5 per cent. When nitre is thrown upon melted silver in a crucible, and the whole retained for about half an hour in fusion, it absorbs 20 times its volume of oxygen, which is given out on plunging the fused metal under a bell jar filled with water.

The analyses of the compounds of silver furnish data from which its

equivalent may be estimated at 108, (108 GMELIN, PHILLIPS, and TURNER: 108.3 GRAHAM: 110 THOMSON.)

REDUCTION OF SILVER ORES. Silver is not unfrequently obtained in considerable quantities from *argentiferous sulphuret of lead*, which is reduced in the usual way, and the argentiferous lead is then fused in a shallow dish, placed in a reverberatory furnace, with a current of air constantly passing over its surface; in this way the lead is converted into *litharge*, and the silver, not being thus oxidized, is left in the metallic state; it is fused in a porous crucible, called a *cupel* or *test*, by which the remaining lead is entirely separated, and a button of pure silver remains. The litharge which results from this operation is afterwards itself reduced by charcoal, and furnishes lead which is almost free from silver, the ordinary lead of commerce generally containing a trace of the latter metal, and being consequently unfit for certain purposes of the arts, especially for the manufacture of white-lead (p. 865). Some of the silver ores, especially the *sulphurets*, are reduced by *amalgamation*. The ore, when washed and ground, is mixed with a portion of common salt and roasted: during this operation sulphate of soda and chloride of silver are formed: the product is then powdered, and agitated with mercury, water, and filings or fragments of iron; in this operation the chloride of silver is decomposed, chloride of iron is formed which is washed away, and the silver and mercury combine into an amalgam, from which the excess of mercury is first squeezed out in leather bags, and the remainder driven off by distillation. The old process of *eliquation* is now scarcely used: it consisted in fusing alloys of copper and silver with lead; this triple alloy was cast into round masses, which were set in a proper furnace upon an inclined plane of iron with a small channel grooved out, and heated red-hot, during which the lead melted out, and in consequence of its attraction for silver, carried that metal with it, the copper being left behind in a reddish-black spongy mass. (AIKIN'S *Dictionary*, Art. SILVER.)

The separation of silver from lead is in many instances facilitated by the process of crystallization. It would appear that where the quantity of silver is comparatively small, it is not simply diffused through the mass of lead, but combined so as to form a definite or atomic alloy, which is as it were merely mixed with the excess of lead. This alloy is more fusible than pure lead, so that when a large quantity of fused lead holding a relatively small proportion of silver, slowly cools, the portion which first solidifies is pure lead, and from this the liquid and argentiferous portion may be poured off: this is again fused, and the same process repeated, so that at last the whole of the silver accumulates in what may be termed the mother-liquor, and this yields an alloy rich in silver, which is ultimately subjected to cupellation.

OXIDES OF SILVER. There are three oxides of this metal, a suboxide Ag_2O , a protoxide AgO , and a binoxide AgO_2 ; of these, the protoxide only forms permanent and definite saline combinations.

SUBOXIDE OF SILVER. Ag_2O . This oxide was first obtained by Faraday, by exposing an ammoniacal solution of the protoxide to the action of air; it separates in the form of a brilliant grey film. (*Quarterly*

Journal, v. 368.) Wöhler obtained it by the action of hydrogen on citrate of silver at the temperature of 212°; the protoxide contained in that salt loses under such circumstances half of its oxygen, and the suboxide remains combined with half of the acid. (*Annalen der Pharm.*, xxx. 1.) “The solution in water of the suboxide salt is dark-brown, and the suboxide is precipitated black from it by potash; when the solution of the subsalt is heated it becomes colorless, and metallic silver appears in it; the salt dissolves of a brown color in ammonia. Several other salts of silver, containing organic acids, comport themselves in the same way as the citrate when heated in hydrogen.” (GRAHAM.)

PROTOXIDE OF SILVER. AgO , may be obtained by adding lime or baryta-water, or dilute solution of pure potassa, to the solution of nitrate of silver, and washing the precipitate. It may also be formed by boiling the moist recently prepared chloride with solution of caustic potassa of the sp. gr. of about 1.3: when the decomposition is effected, the resulting oxide is entirely soluble in dilute nitric acid. Its specific gravity is about 7.2. It is of a very dark olive color, anhydrous, tasteless, but soluble to a small extent in pure water free from saline matter, and, like oxide of lead, has when in solution an alkaline reaction: this solution is reddened by exposure to light; and is rendered turbid by a little carbonic acid, but again becomes clear with excess. When heated to dull redness it is reduced to the metallic state; long exposure to light also reduces it, converting it into a black powder, which is either silver or its suboxide. It is reducible by hydrogen at a temperature of about 212°; and also by hypophosphorous, phosphorous, and sulphurous acids: (imperfectly by the latter, into sulphate, and metal.) (VOGEL.) When moistened with water it is reduced by zinc, cadmium, tin, and copper, but not by iron or mercury. (FISCHER, *Poggend.*, x. 605.) It confers a yellow color upon glass, and is employed in enamel and porcelain painting. It consists of

						Berzelius.		Davy.		Gay Lussac and Thenard.
Silver	1	108	93.103	93.112	93.1 92.937
Oxygen	1	8	6.897	6.888	6.9 7.063
<hr/>										
Protoxide of silver	1		116		100.000		100.000		100.0	100.000

PEROXIDE OF SILVER. AgO_2 . Ritter, by electrizing a weak solution of silver, observed the deposition of acicular crystals at the positive pole, which, according to Grotthuss, dissolve in nitric acid without decomposition, and are a *peroxide of silver*. Ammonia energetically decomposes this compound, and sulphuric and phosphoric acids convert it into the protoxide. (*Gehlen's Journ.*, iii.) When mixed with phosphorus or sulphur, and struck with a hammer, it detonates. (According to Fischer and Gmelin, (*Handbuch*, iii. 602,) the crystals obtained by the electrolysis of a solution of nitrate of silver, after having been carefully washed and dried, yield when heated, fumes of nitrous acid, and cold water abstracts nitrate of silver from the residue: Gmelin suspects them to be a nitrate of the peroxide.)

AMMONIURET OF SILVER. ARGENTATE OF AMMONIA. Oxide of silver readily dissolves in solution of ammonia, forming a colorless liquor, which,

as above stated, becomes coated with a film of suboxide by exposure to air, and when kept for some months in a stopped bottle, acquires a film of metallic silver. When oxide of silver recently precipitated from the nitrate by lime water, and deprived of adhering moisture by bibulous paper, is acted upon by very strong aqueous solution of ammonia, it is converted into *Berthollet's fulminating silver*. (*Crell's Annals*, 1788.) The best process for preparing it is to pour a small quantity of strong aqueous ammonia upon the oxide; a portion is dissolved, and a black powder remains, which is the detonating compound. It is also formed by adding pieces of pure caustic potassa to a solution of chloride of silver in strong aqueous ammonia, as long as effervescence ensues: the black turbid liquor is poured upon a filter, on which the fulminating silver is collected, and whilst moist should be carefully divided into small portions on filtering paper, and allowed to dry. This compound explodes with tremendous violence when gently rubbed or heated; nitrogen and water are instantaneously evolved, and the silver is reduced. The oxide of silver should be perfectly pure and thoroughly edulcorated, and the ammonia quite free from carbonic acid, and it should only be prepared in small quantities, and handled with the greatest caution, for it occasionally explodes even while still wet. It is soluble in ammonia, and this solution sometimes deposits it in small brilliant opaque crystals. It is immediately decomposed by hydrochloric acid, which forms chloride of silver and sal-ammoniac; and by sulphuretted hydrogen, which forms sulphuret of silver and hydrosulphuret of ammonia; with sulphuric acid, it affords sulphate of silver, and of ammonia, but nitrogen is also evolved. There is some doubt respecting the real nature of this fulminating compound, and it appears not improbable that it may be a nitruet or nitride of silver, $= \text{Ag}_3 \text{N}$. It is by some regarded as an amide.

CHLORIDE OF SILVER. AgCl . When silver leaf is acted upon by gaseous chlorine it is gradually converted into this compound, and if sufficiently thin, a leaf of chloride of silver is obtained; otherwise the action is superficial, and the metal beneath is protected by the exterior film of chloride. When dry hydrochloric acid gas is passed over red-hot silver, chloride of silver is formed, and hydrogen liberated; and on the other hand, when hydrogen is passed over red-hot chloride of silver, hydrochloric acid is formed, and the silver reduced to the metallic state. (BOUSSINGAULT, *Ann. Ch. et Ph.*, liv. 260.) This apparently anomalous action is probably analogous to the cases formerly adverted to, of the decomposition of steam by iron, and of oxide of iron by hydrogen, (p. 138.)

Chloride of silver is usually procured by adding a solution of chlorine, of hydrochloric acid, or of common salt, to a solution of nitrate of silver, or, indeed, to any of the soluble salts of silver, with the exception of the hyposulphite. It falls in the form of a curdy precipitate, of a white color, but which, by exposure to light, becomes violet-colored, brown, and ultimately black (in consequence of the formation in the first instance of a *subchloride of silver*?) This happens even in diffused daylight, but in sunshine the change is extremely rapid, more especially if any trace of organic matter be present. This property of the chloride has led to its

application for purposes of photogenic drawing. (See *Nitrate of Silver*.) When a small quantity of subchloride of mercury is precipitated along with the chloride of silver, the blackening effect of light is greatly diminished. Chloride of silver is perfectly insoluble in water; so that the minutest portion of hydrochloric acid, or of any chloride in aqueous solution, may be detected by adding to the liquid a drop or two of nitrate of silver; it becomes opalescent, and grey or brown by exposure to light. It is sparingly dissolved by concentrated hydrochloric acid, and thrown down upon dilution: when the hydrochloric solution is carefully evaporated, the chloride is deposited in the form of octohedral crystals: even diluted hydrochloric acid will dissolve a little chloride of silver: a solution of 1 part of nitrate of silver in 15,000 of water becomes slightly milky with a little hydrochloric acid, but when more is added, it again becomes transparent: sulphuretted hydrogen however discolours this transparent solution. (REINSCH, *Journ. prakt. Chem.*, xiii. 133.) It is insoluble in nitric acid, and in cold sulphuric acid, but when boiled in sulphuric acid, it is very slowly decomposed with the evolution of hydrochloric acid, and formation of sulphate of silver: a trace of the chloride is also retained in solution by boiling sulphuric acid, but falls on cooling. (VOGEL.) When dry chloride of silver is heated to dull redness in a silver crucible, it does not lose weight, but fuses, and, on cooling, concretes into a grey semitransparent substance, (sp. gr. 5.45,) which has been called *horn silver* or *luna cornea*. Its melting point is 500° . (GME-LIN.) If slowly cooled, Proust has remarked that it has a tendency to octohedral crystallization. Heated to a bright red or white-heat in an open vessel, it volatilizes in dense white fumes. Scheele was the first who examined the cause of the blackening effect of light upon this chloride, and the curious results of his researches have already been referred to (p. 102). He found that the metal was partially reduced, and hydrochloric acid formed; hence moisture is necessarily present. Seebeck found that white chloride of silver might be exposed, without change of color, when covered in a stopped phial, with sulphuric acid; but if the phial was open, the blackening ensued; as it did also when water was added. When light is carefully excluded, it appears that perfectly pure hydrogen does not discolour this chloride.

If fused with twice its weight of potassa or soda, chloride of silver is decomposed, and a globule of metallic silver is obtained. This reduction is best effected by projecting the dry chloride upon twice its weight of fused carbonate of potassa, or upon the fused mixture of the carbonates of potassa and soda. Moist chloride of silver is also decomposed when triturated with, and then boiled in a strong solution of caustic potash, (sp. gr. 1.25 to 1.3.) Dr. Gregory, as has been above stated, recommends this as a good mode of obtaining oxide of silver, which, when the decomposition is complete, remains as a heavy black powder. (*Proc. Chem. Soc.*, Jan. 1843.)

When carbonic oxide is passed over red-hot chloride of silver, chloro-carbonic acid is formed, and the silver reduced. $\text{AgCl} + \text{CO} = \text{Ag} + \text{CO}, \text{Cl}$. Heated with phosphorus it is imperfectly reduced, and chloride of phosphorus is formed: gently heated in a stream of phosphuretted hydrogen, hydrochloric acid, phosphorus, and silver, are the results. It is also

decomposed, when moist, by zinc, tin, lead, iron, copper, mercury, and some other metals, especially if aided by heat and by a little hydrochloric acid. Triturated with fine zinc filings and moistened, the heat produced is so considerable as to fuse the resulting alloy of zinc and silver. (FARADAY, *Quarterly Journal of Science and Arts*, viii. 374.) When a lump of chloride of silver is put with zinc or iron filings into diluted sulphuric acid, the reduced silver retains the original form of the chloride, the evolved hydrogen therefore appears to be the reducing agent. Chloride of silver is not reduced when heated with pure carbon, but the ordinary charcoals decompose it in consequence of their containing hydrogen. According to Ricker, chloride of silver may be best reduced by mixing it with about its weight of powdered charcoal, and twice its weight of nitre, and conveying the mixture in small portions, but quickly one after another, into a sufficiently large red-hot crucible, afterwards kept for a quarter of an hour at a red-heat, when the metal may be poured out. "The easiest and quickest mode of reducing chloride of silver is to mix it with one-third its weight of rosin and one-twelfth of nitre; heat it to a cherry-red in a Hessian crucible for ten minutes, then quickly raise it to a white-heat for about twenty minutes, when it may be poured out, or remain till cold at the bottom of the crucible." (DECK.) Chloride of silver is rapidly reduced when boiled in a solution of caustic potassa, to which some sugar has been added; carbonic acid is evolved, and the metallic silver separates in a pulverulent form. (LEVOL.)

Chloride of silver is very soluble in ammonia, a circumstance by which it is usefully distinguished from some other chlorides, which, like it, are white, and formed by precipitation; we should be cautious in applying heat to the ammoniacal solution, as it sometimes forms a precipitate of fulminating silver, and furnishes crystals which are explosive, and which, when exposed to air, or put into water, lose their transparency, evolve ammonia, and crumble into chloride of silver. The fused chloride, exposed to ammoniacal gas, absorbs a considerable portion, which is given off by heat. If the dry chloride, thus saturated with ammonia, be thrown into chlorine, the ammonia spontaneously inflames. (FARADAY, *Journal of Science and Arts*, v. 75.) Chloride of silver is soluble in and decomposed by all the liquid hyposulphites: it is also soluble in a solution of sal-ammoniac, and of the chlorides of potassium and sodium, and these solutions may be used in the process of silvering copper or other metals: they afford double chlorides on evaporation, which may be obtained crystallized, but which have not been examined in detail: they are decomposed by water.

As chloride of silver is insoluble in water, and very readily formed, it is often employed in quantitative analysis, as a means of ascertaining the proportion of chlorine present in various compounds. In these cases some excess of the precipitant should be used, and the precipitate allowed to subside previous to separating it upon the filter: if the supernatant liquor become perfectly clear, the whole of the silver has fallen; if it remain opalescent, a portion is probably still retained. When the precipitate remains long suspended, its deposition may be accelerated by heat, or by adding a little nitric acid. The chloride in these cases should be perfectly dried in a silver crucible, up to incipient fusion.

Chloride of silver consists of

						Buchholz.	Rose.	Wenzel and Berzelius.	Gay Lussac.	Marcet and J. Davy.	Turner.					
Silver	1	108	75	75.18	75.33	75.25	75.5	75.3
Chlorine	1	36	25	24.82	24.67	24.75	24.5	24.7
Chloride of silver	}	1		144		100		100.00		100.00		100.00		100.0		100.0

Native Chloride of Silver has been found in most of the silver-mines; it occurs massive and crystallized in small cubes and octohedra.

AMMONIO-CHLORIDE OF SILVER. $3\text{NH}_3, 2\text{AgCl}$. This compound, above mentioned as having been formed by Faraday, has been more specially examined by H. Rose. (*Poggend.*, xx. 157.) He finds it composed of

							II. Rose.
Ammonia	3	...	51	...	15.04	...	14.97
Chloride of silver	2	...	288	...	84.96	...	85.03
<hr/>							
Ammonio-chloride of silver	1		339		100.00		100.00

CHLORIDE OF AMMONIUM AND SILVER. $\text{NH}_4\text{Cl}, \text{AgCl}$. This compound was obtained by Vogel in transparent acicular crystals by saturating a boiling solution of sal-ammoniac with chloride of silver.

CHLORATE OF SILVER. AgO, ClO_5 , is formed by digesting oxide of silver in chloric acid: it forms small rhombic crystals, which, by the action of chlorine, are converted into chloride of silver. They are soluble in 4 parts of water at 60° . (CHENEVIX. VAUQUELIN.) In 5 of cold water, and also soluble in alcohol. (WAECHTER.) They fuse at 446° , and at 518° give off oxygen and a trace of chlorine: heated rapidly they explode, and when mixed with combustibles, detonate violently under the blow of a hammer. Chlorate of silver is also formed by passing chlorine through water in which oxide of silver is suspended, but is afterwards decomposed, chloride of silver and chloric acid (but no perchloric acid) being formed. By the action of hyperchlorous acid on oxide of silver, or on finely-divided silver, no chloric acid is formed, but a mixture of peroxide and chloride of silver. By dissolving chlorate of silver in ammonia, prismatic crystals readily soluble in water and ammonia, are formed on evaporation, $= \text{AgO}, \text{ClO}_5, 2\text{NH}_3$. They melt at 212° , giving off ammonia and leaving chlorate of silver: rapidly heated, they decompose with explosion and light: potassa added to a solution of this salt, throws downs Berthollet's fulminating silver.

PERCHLORATE OF SILVER. AgO, ClO_7 , is obtained in the form of a white powder, by slowly evaporating the solution of oxide of silver in aqueous perchloric acid. When this salt is fused, it concretes into a crystalline mass on cooling, which is deliquescent and soluble in alcohol: it deflagrates when heated nearly to redness. (SERULLAS, *Ann. Ch. et Ph.*, xxxvi. 307.)

IODIDE OF SILVER. AgI . When silver leaf is put into a bottle containing a little iodine it is speedily tarnished, and in the course of a few

days converted into a film of iodide. Iodide of silver is precipitated upon adding hydriodic acid, or a soluble iodide, to a solution of nitrate of silver. It is of a dingy-yellowish color, insoluble in water, and decomposed when heated with potassa. It is nearly insoluble in ammonia. When fused at a dull red-heat it acquires a red color. It volatilizes before the blowpipe, leaving a little silver only behind. It is discolored by light. Concentrated nitric and sulphuric acid decompose it. It dissolves in concentrated solutions of the alkaline chlorides, and combines also with iodide of potassium and other alkaline and earthy iodides. A thin film of iodine upon a plate of silver is used in Daguerre's photographic process, the plate of silvered copper intended to receive the image in the camera being prepared by exposing it in a box containing iodine: the light seems to act upon this film rather than upon an iodide of silver. According to Claudet the sensibility of the plates to the influence of light is greatly enhanced by the use of chloride of iodine, instead of iodine only. (*Proc. R. S.*, June 10, 1841.) The effects of light upon paper embued with iodide of silver have been described by Talbot. (*Phil. Mag. and Journ.*, xii. 258. In reference to the use of iodine and iodic compounds in photogenic drawing, see SIR J. HERSCHEL, *Phil. Trans.*, 1840: also MR. R. HUNT's and MR. ALFRED TAYLOR's *Pamphlets*: also the preceding section on the chemical effects of light, page 100.)

Iodide of silver consists of

Silver	1	108	46·15
Iodine	1	126	53·85
<hr/>					
Iodide of silver	1		234		100·00

Native Iodide of Silver has been found in some of the Mexican ores, associated with native silver, sulphuret of lead, and carbonate of lime: it was analyzed by treating it first with acetic acid, which abstracted the carbonate of lime; then by nitric acid, to remove the native silver and leave a mixture of sulphate of lead with the iodide of silver: the latter is decomposed by heating it a current of dry chlorine; chloride of iodine passes off and chloride of silver remains. (VAUQUELIN, *Ann. Ch. et Ph.*, xxix. 99. DUMAS.)

AMMONIO-IODIDE OF SILVER. $2\text{NH}_4\text{I}, \text{AgI}$, is a deliquescent salt obtained by dissolving iodide of silver in solution of iodide of ammonium. (POGGIALE.)

IODATE OF SILVER. AgO, IO_5 , is precipitated in the form of a white powder by adding iodic acid or iodate of potassa to a solution of nitrate of silver. It is very soluble in aqueous ammonia, and is deposited from this solution in small rectangular prisms, which retain no ammonia: sulphurous acid added to this ammoniacal solution, throws down iodide of silver, and becomes sulphuric acid. (GAY LUSSAC.) Iodate of silver is difficultly soluble in nitric acid: it is resolved by hydrochloric acid into chloride of silver, terchloride of iodine, water, and chlorine: $\text{AgO}, \text{IO}_5 + 6\text{HCl} = \text{AgCl} + \text{ICl}_3 + 6\text{HO} + 2\text{Cl}$. (GMELIN, *Handbuch*. RAMMELSBURG, *Poggend.*, xlv. 572: BENCKISER, *Ann. der Pharm.*, xvii. 255.) It consists of

						Benckiser.
Oxide of silver	1	116	41.13 40.57
Iodic acid	1	166	58.87 59.43
<hr/>						<hr/>
Iodate of silver....	1		282		100.00	100.000

PERIODATE OF SILVER. When a solution of bibasic periodate of soda in dilute nitric acid is dropped into a solution of nitrate of silver, a pale greenish-yellow precipitate falls, which, when dissolved in warm dilute nitric acid, crystallizes on cooling in pale yellow hydrous crystals = $\text{AgO}, \text{IO}_7 + 3\text{HO}$. When these crystals are dissolved in warm nitric acid, the solution deposits orange-colored crystals of anhydrous neutral periodate = AgO, IO_7 . (AMMERMÜLLER and MAGNUS. *Poggend.*, xxviii. 516.)

BROMIDE OF SILVER. AgBr , is an insoluble yellowish substance thrown down upon the addition of bromine, or hydrobromic acid, or the soluble bromides, to nitrate of silver: it dissolves in strong aqueous solution of ammonia, (BALARD, *Ann. de Ch. et Ph.*, xxxii. 361): it is fusible, and concretes on cooling into a yellow corneous mass, sp. gr. 6.3: it crystallizes in octohedra from its hydrobromic solution. In a moist state it acquires a grey tint by exposure to light: chlorine converts it into chloride of silver: it is sparingly soluble in solutions of bromide of potassium and sodium, and more abundantly so in solution of sal-ammoniac: it consists of

						Balard.
Silver	1	108	58 58.9
Bromine	1	78	42 41.1
<hr/>						<hr/>
Bromide of silver	1		186		100	100.0

Native bromide of Silver, has been found in Mexico and Chili, and at Huelgoeth in France: in appearance it bears resemblance to the native chloride, but its color is yellow-green, and it is in small cubic crystals. (BERTHIER, *Ann. Ch. et Ph.*, 3 Ser. ii. 417, and iv. 164.)

BROMATE OF SILVER. AgO, BrO_5 , falls in the form of a white insoluble powder on adding aqueous bromic acid or bromide of potassium to solution of nitrate of silver: it becomes grey by exposure to light: it is soluble in ammonia, but not in nitric acid. (RAMMELSBERG, *Poggend.*, lii. 94.)

FLUORIDE OF SILVER is a soluble compound, which does not crystallize. When heated it fuses; and at a higher temperature, and exposed to air, it is slowly reduced. (BERZELIUS, *Ann. Ch. et Ph.*, xi. 121.)

NITRITE OF SILVER. This salt is obtained by boiling powdered silver in nitric acid already saturated with silver: or nitrate of soda may be fused till converted into nitrite, when it precipitates silver brown; if this salt be then dissolved in boiling water, precipitated by nitrate of silver, and the solution filtered while hot, nitrite of silver separates as the solution cools; it requires 120 parts of water at 60° for its solution. (PROUST. *Nicholson's Journal*, xv. 376. HESS. *Poggend.*, xii. 261.)

NITRATE OF SILVER. AgO, NO_5 . Nitric acid, diluted with 3 parts of water, readily dissolves silver, with the disengagement of nitric oxide gas. If the acid contain the least portion of hydrochloric acid, the solution will be turbid, and deposit a white precipitate; and if the silver contain copper, it will have a permanent bluish hue; or if gold, that metal will remain undissolved in the form of a black powder.

The solution of nitrate of silver should be perfectly clear and colorless; it is caustic, and tinges animal substances of a deep yellow, which, by exposure to light, becomes a deep purple, or black stain, and is indelible, or peels off with the cuticle: it consists of reduced silver. Nitrate of silver may be obtained in white anhydrous crystals, in the form of four and six-sided tables or thin plates: by slow evaporation it forms right rhombic prisms. (BROOKE, *Ann. of Phil.*, 2nd Series, vii. 162.) Their specific gravity is 4.35. They have a bitter and metallic taste, and are soluble in about their own weight of water at 60° , and half their weight at 212° : they are insoluble in nitric acid, and this acid added to an aqueous solution of nitrate of silver, throws down a crystalline precipitate of the salt. Alcohol also dissolves about one-fourth its weight of this salt at its boiling-point, but deposits nearly the whole as it cools. The aqueous solution of this salt is neutral to the test of litmus.

Nitrate of silver blackens when exposed, under ordinary circumstances, to light, and when thus acted upon, is no longer perfectly soluble in water, owing to the separation of a portion of metallic silver; but if cautiously excluded from the contact of organic matter, light alone does not discolor it: according to Filiere, when the crystals are wrapped in paper they are gradually reduced to the metallic state. (*Ann. Ch. et Ph.*, LXii. 335.) When heated in a silver crucible it fuses into a grey mass, and if cast into small cylinders, forms the *lunar caustic* of pharmacy; the *argenti nitras* of the *Pharmacopœia*. In forming this preparation, care should be taken not to overheat the salt, so as to blacken it, and the moulds should be warmed. This preparation is sometimes adulterated with nitrates of potassa, zinc, lead, or copper: the mode of detecting the three last-named metals will be evident from previous statements: the adulteration with nitre may be inferred from the result of the decomposition of the salt by red-hot charcoal: pure fused nitrate of silver ignited by the blow-pipe in a small cavity of a piece of dense charcoal leaves about 63 *per cent.* of pure silver. Exposed to a red-heat, the acid is partly evolved and partly decomposed, and metallic silver obtained. Sulphur, phosphorus, charcoal, hydrogen, and several of the metals, decompose this nitrate. A few grains mixed with a little sulphur, and struck upon an anvil with a heavy hammer, produce a detonation; phosphorus occasions a violent explosion when about half a grain of it is placed upon a crystal of the nitrate, upon an anvil, and struck sharply with a hammer; and if heated with charcoal it deflagrates, and the metal is reduced.

If a piece of silk dipped into a solution of nitrate of silver be exposed, while moist, to a current of hydrogen gas, it is first blackened, and afterwards becomes iridescent from the reduction of portions of the metal. (MRS. FULHAME'S *Essay on Combustion*.) Ivory, marble, and several other bodies, may be stained black, or even silvered, by soaking them in a solution of nitrate of silver, and fully exposing them to the action of the sun's rays. When the vapor of pure distilled water is made to pass

through nitrate of silver, the solution assumes all the shades between yellow and dark-brown, according to its concentration and the time the steam has passed through it. When it has acquired the temperature of 212° , its color increases rapidly. Nitric acid immediately destroys this color, the cause of which is referred by Pfaff to the deoxidizing agency of the steam. (*Quarterly Journal*, xvi. 162.) A stick of phosphorus, introduced into a solution of nitrate of silver, soon becomes beautifully incrustated with the metal, which separates upon it in arborescent crystals. A plate of copper occasions a brilliant precipitation of crystalline silver, and the copper is oxidized and dissolved by the acid. Mercury introduced into the solution of nitrate of silver, causes a beautiful crystalline deposit of silver, called the *arbor Dianæ*: it was first remarked by Lemery. To obtain this crystallization in its most perfect state, the solution should contain a little mercury, and the mercury put into it should be alloyed with a little silver. Baumé directs an amalgam of 1 part of silver with 7 of mercury, of which a small piece is to be introduced into a solution composed of 6 drachms of saturated nitrate of silver and 4 drachms of a similar solution of mercury diluted with 5 ounces of distilled water: a small flask or matrass should be used for the experiment, kept perfectly at rest: in a few minutes small filaments of silver darken the surface of the amalgam, and in about eight and forty hours the whole has separated in a shrub-like form. The addition of mercury to the solution, and of silver to the precipitating mercury, is said to give a degree of tenacity to the arborescent deposit of crystals, which prevents their falling to the bottom of the flask.

The alkaline metallic oxides decompose nitrate of silver; it is also decomposed by hydrochloric, sulphuric, phosphoric, and boracic acids. The protosulphate of iron throws down metallic silver when added to a solution of the nitrate; protochloride of tin forms a grey precipitate, consisting of peroxide of tin and oxide of silver. Ammonia, added to solution of nitrate of silver, occasions a precipitate, soluble in excess of the alkali.

Nitrate of silver is employed for writing upon linen, under the name of *indelible* or *marking ink*, which may be prepared by dissolving 2 drachms of pure nitrate of silver and 1 drachm of gum arabic in 7 drachms of distilled water, colored by a little China ink. The preparatory liquid for moistening the cloth is made by dissolving 2 ounces of crystallized carbonate of soda and 2 drachms of gum arabic in 4 ounces of water. "For this ink, which is expensive, another liquid has been substituted by bleachers, namely, coal tar made sufficiently thin with naphtha to write with, which is found to resist chlorine, and to answer well as a marking ink." (GRAHAM.) Nitrate of silver is an ingredient in some of the liquids which are sold for the purpose of changing the color of hair: the black stain of any of these preparations of silver may be removed by cyanide of potassium. It is used in medicine; and in surgery, as an excellent caustic. When taken internally, a very disagreeable effect frequently follows its use, which is the discoloration of the *rete mucosum*; so that the whole surface of the body, and especially the parts most exposed to light, acquire a leaden-grey or livid color, which is permanent, and can neither be removed nor prevented by any means yet tried: it is not improbable, however, that some of the cyanides might be

effectual, or that cyanide of silver might be employed medicinally without the blackening effect.

Solution of nitrate of silver is a valuable test of the presence of chlorine, hydrochloric acid, and the soluble chlorides, with which it forms a white cloud when very dilute, but a flaky precipitate when more concentrated; the precipitate is soluble in ammonia, but insoluble in nitric acid. Heat, agitation, or the addition of a few drops of nitric acid, so as to render the liquid sour, facilitate the deposition of the precipitate. The hydriodic, hydrobromic, and hydrocyanic acids, also occasion precipitates in solution of nitrate of silver, which become discolored by exposure to light. Its application as a test for arsenic and arsenious acids has already been noticed. Gallic and tannic acid, and the varieties of extractive matter, discolor nitrate of silver without the aid of light. A peculiar extractive matter sometimes occurs in rough nitre, which also causes its solution to blacken nitrate of silver, and some spring and mineral waters produce a similar effect.

Nitrate of silver is an anhydrous salt, composed of

						Proust.	
Oxide of silver	1	...	116	...	68.24	...	69.5
Nitric acid	1	...	54	...	31.76	...	30.5
<hr/>			<hr/>		<hr/>		<hr/>
Nitrate of silver	1		170		100.00		100.0

AMMONIO-NITRATE OF SILVER. Ammonia is rapidly absorbed by nitrate of silver, with the production of heat sufficient to fuse the compound, which is white, coherent, and consists of 100 parts of the nitrate + 29.5 ammonia. Mitscherlich has described an analogous compound formed in the humid way. (*Ann. de Ch. et Ph.*, lxii. 314; *Poggend. Ann.*, ix. 413.) An ammonio-nitrate of silver is also obtained when ammonia is added to a solution of nitrate of silver till the first-formed precipitate is entirely redissolved. This solution forms a good marking ink, and has also been used in the preparation of paper for photogenic drawing, and as a test for arsenic.

SULPHURET OF SILVER. AgS . Silver readily combines with sulphur, and produces a grey crystallizable compound, considerably more fusible and much softer than silver. It may be obtained by heating finely-divided silver or plates of silver with sulphur. Its density is about 6.8 to 7.

Sulphuretted hydrogen and hydrosulphuret of ammonia occasion a copious black precipitate of sulphuret of silver when added to solutions of the metal: sometimes a portion of the silver is apparently at the same time reduced to the metallic state. It is the presence of some form of sulphur in the atmosphere, generally sulphuretted hydrogen, which occasions the tarnish upon exposed silver, and which, though only superficial, is a great obstacle to many applications that might otherwise be made of this beautiful metal. Sulphuret of silver is not decomposed by a solution of chloride of copper except common salt be added, in which case, chloride of silver and sulphuret of copper are formed; 100 parts of sulphuret of silver are thus convertible in the course of a few days into about 146 parts of a mixture of chloride and sulphuret. Half the sulphuret of silver is first decomposed, and yields, with the chloride of copper, chloride of silver, sulphur, and dichloride of copper, which

latter remains dissolved with the common salt: $\text{AgS} + 2\text{CuCl} = \text{AgCl} + \text{S} + \text{Cu}_2\text{Cl}$. Then the dichloride of copper dissolved in the solution of common salt, acts upon the other half of the sulphuret of silver, forming chloride of silver and disulphuret of copper: $\text{AgS} + \text{Cu}_2\text{Cl} = \text{AgCl} + \text{Cu}_2\text{S}$: hence a solution of dichloride of copper in chloride of sodium also decomposes sulphuret of silver. (BOUSSINGAULT, *Ann. Ch. et Ph.*, LI. 350. GMELIN, *Handbuch*.) Sulphuret of silver consists of

					Vauquelin.	Berzelius.	Wenzel.	Klaproth. <i>Native.</i>
Silver	1	108	87.097	87.27	87.032	85.5	85	
Sulphur	1	16	12.903	12.73	12.968	14.5	15	
<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	
Sulphuret of silver	1	124	100.000	100.00	100.000	100.0	100	

Native Sulphuret of Silver, or *vitreous silver-ore*, is found in various forms, and when crystallized is in cubes, octohedra, and dodecahedra. It is soft and sectile. The finest specimens are from Siberia. The method of its reduction has been above described. A triple combination of *silver*, *antimony*, and *sulphur*, constitutes the *red* or *ruby silver-ore*; it is found massive and crystallized in hexahedral prisms. It consists of about 70 parts of sulphuret of silver, and 30 of sulphuret of antimony; or, according to Bonsdorff, of 3 atoms of silver, 2 of antimony, and 6 of sulphur. It occurs in all the silver-mines, and is sometimes accompanied by the *brittle sulphuret of silver*, or *silver glance*, and by *antimonial silver*: Ag_2Sb .

HYPOSULPHITE OF SILVER. $\text{AgO}, \text{S}_2\text{O}_2$, has been examined by Herschel. (*Edin. Phil. Journal*, i. 26; ii. 154.) It is formed by dropping a weak solution of nitrate of silver into a very dilute solution of hyposulphite of soda: a white cloud is at first produced, which redissolves on agitation; on adding more of the precipitant, the cloud reappears and aggregates into a grey precipitate, which appears to consist of hyposulphite of silver; the supernatant liquor tastes intensely sweet, which is remarkable, considering the disgusting bitterness both of the nitrate and of the hyposulphite, and shows, "how little we know of the way in which bodies affect the organs of taste. Sweetness and bitterness, like acidity, seem to depend upon no particular principle, but to be regulated by the state of combination in which the same principles exist at different times." Hyposulphite of silver is also produced when chloride of silver is dissolved in any of the hyposulphites; the solution is intensely sweet without any metallic flavor. These facts show the strong affinity that exists between oxide of silver and hyposulphurous acid. The solubility of argentine compounds in hyposulphites has led to an important application of them in photogenic drawing, for the purpose of fixing the designs, by the removal of all adhering or unchanged salt of silver. (See HERSHEY, A. TAYLOR, &c.) Hyposulphite of silver is very prone to decomposition, so as to form sulphate of oxide of silver, and sulphuret of silver; hence the occasional blackening of its solutions.

HYPOSULPHITE OF AMMONIA AND SILVER. When a solution of chloride of silver in hyposulphite of ammonia is mixed with alcohol, a precipitate falls which is probably $2[\text{NH}_3, \text{S}_2\text{O}_2] + \text{AgO}, \text{S}_2\text{O}_2$: the remaining liquid yields, on evaporation, six-sided prisms of the same salt: it is so

sweet as to communicate a perceptible sweet flavor to 32,000 parts of water. If excess of chloride of silver be added to solution of hyposulphite of ammonia, a white and almost insoluble crystalline powder is formed, which soon blackens from the formation of sulphurous acid and sulphuret of silver: it appears to be $\text{NH}_3, \text{S}_2\text{O}_2, + \text{AgO}, \text{S}_2\text{O}_2$: it yields a very sweet solution with aqueous ammonia. (HERSCHEL.)

HYPOSULPHITE OF POTASSA AND SILVER is formed when liquid potassa is dropped into the solution of chloride of silver in hyposulphite of soda; it separates in the form of a copious precipitate, which, when washed and dried, is found to consist of small grey pearly scales; they are difficultly soluble in water; of a very sweet taste; and, heated before the blow-pipe, afford a bead of silver. Several other analogous double salts have been described by Herschel.

HYPOSULPHITE OF SODA AND SILVER. By evaporating a solution of chloride of silver in hyposulphite of soda, crystals are obtained $= 2[\text{NaO}, \text{S}_2\text{O}_2] + \text{AgO}, \text{S}_2\text{O}_2$. The same salt is formed, according to Lenz, in lamellar crystals by saturating a concentrated solution of hyposulphite of soda with chloride of silver, filtering, precipitating by alcohol, washing the precipitate with alcohol, and drying it in vacuo. (*Ann. der Pharm.*, XL. 94.) It is unaltered at common temperatures by air and light: heated to 212° it gradually darkens from formation of sulphuret of silver. The crystals contain 2 atoms of water. When a neutral solution of nitrate of silver is added to a solution of hyposulphite of soda till a precipitate forms, a dirty white crystalline powder is obtained $= \text{NaO}, \text{S}_2\text{O}_2 + \text{AgO}, \text{S}_2\text{O}_2, + \text{HO}$. (LENZ.) Similar double salts with lime and with strontia have been described by Herschel.

SULPHITE OF SILVER. AgO, SO_2 , is obtained in crystalline grains by digesting oxide of silver in sulphurous acid, or by adding an alkaline sulphite to a solution of silver. It produces double salts with the sulphites of the alkalis. According to Fourcroy, it is not blackened by exposure to light, nor altered by air. When sulphurous acid or alkaline sulphites are added to nitrate of silver, a beautifully white sulphite is thrown down, and only a small portion of silver remains in solution. Sulphite of silver is insoluble in water, and nearly so in sulphurous acid; it is not decomposed by acetic acid, but the more powerful acids expel the sulphurous: it is soluble in ammonia. When boiled in water, or when dried at 212° , it is converted into sulphate and metal: when an alkaline sulphite is added to the water in which it is boiling, it is easily and entirely reduced. When an ammoniacal solution of chloride of silver to which sulphite of ammonia has been added is kept boiling, the whole of the silver is precipitated in the metallic state as a dull brownish-white powder. On boiling fresh and moist chloride of silver in a solution of an alkaline sulphite, it is also decomposed into metallic silver; to obtain this silver perfectly pure, it must, however, be washed in ammonia. (BERTHIER.)

HYPOSULPHATE OF SILVER, $\text{AgO}, \text{S}_2\text{O}_5$, is formed by digesting carbo-

nate of silver in hyposulphuric acid: it crystallizes in permanent prismatic crystals, soluble in 2 parts of cold water, and containing 2 equivalents of water of crystallization; they blacken when exposed to light, and fall, when gently heated, into a grey powder, which leaves a little sulphuret of silver when dissolved in boiling water. (HEEREN.)

HYPOSULPHATE OF SILVER AND AMMONIA. On cooling a hot saturated solution of hyposulphate of silver in ammonia, brilliant rhombic prisms are obtained, soluble in water without decomposition, and becoming grey by exposure to light: exposed to heat they afford water, ammonia, a sublimate of sulphite of ammonia, some sulphurous acid, and sulphate of silver: their formula is $\text{NH}_3, \text{AgO} + \text{NH}_4 \text{O}, \text{S}_2 \text{O}_5$. (RAMMELSBERG, *Poggend.*, LViii. 295. See also in reference to this double salt, HEEREN, *Poggend.*, vii. 192.)

SULPHATE OF SILVER, AgO, SO_3 , is deposited when sulphate of soda is mixed with nitrate of silver. It is also formed by boiling silver with its weight of sulphuric acid. It forms a white saline mass, easily fusible. It requires about 90 parts of water at 60° for its solution; in boiling water it is more soluble, and is deposited, as the solution cools, in small anhydrous prismatic crystals: it is decomposed at a red-heat, and leaves metallic silver: it dissolves in sulphuric acid, and on moderate dilution the greater part of the salt again falls down; the best crystals of sulphate of silver are obtained from its solution in diluted sulphuric acid, or according to Mitscherlich, from its solution in nitric acid. By leaving a strong sulphuric solution of silver in a dark place it gradually absorbs water, and octohedral crystals of the sulphate are deposited in it. The specific gravity of sulphate of silver is 5.34. (KARSTEN.) Vogel has stated that finely divided silver is dissolved by anhydrous sulphuric acid, without the evolution of sulphurous acid: the conditions of this action have not been ascertained.

Upon the large scale, small portions of gold may be most economically separated from large quantities of silver, by heating the finely granulated alloy in sulphuric acid: the gold remains in the form of a black powder, and the sulphate of silver may be decomposed by the action of metallic copper; the silver is precipitated in a pulverulent state, and, with a little borax or other vitrifiable flux, is fused, and cast into ingots: the sulphate of copper is easily obtained in the crystallized state by evaporating the residuary liquid.

A compound acid, which may be called *nitrosulphuric*, consisting of 1 part of nitre dissolved in about 10 of sulphuric acid, dissolves silver at a temperature below 200° , and the solution admits of moderate dilution before sulphate of silver separates from it. This acid scarcely acts upon copper, lead, or iron, unless diluted with water; it is, therefore, useful in separating the silver from old plated articles; the silver may afterwards be obtained either in the form of chloride, by adding common salt, or by diluting the acid and continuing the immersion of the pieces of copper which have lost their silvering, and which will now dissolve in the diluted acid, and occasion the precipitation of metallic silver. (KEIR, *Phil. Trans.*, LXXX.)

Sulphate of silver consists of

Oxide of silver	1	116	74.36
Sulphuric acid	1	40	25.64
<hr/>					
Sulphate of silver.....	1		156		100.00

AMMONIO-SULPHATE OF SILVER. 100 parts of sulphate of silver slowly absorb 11.82 of dry ammonia. (H. ROSE, *Ann. Ch. et Ph.*, LXII. 314.) In the humid way, Mitscherlich formed a double salt containing twice as much ammonia: he saturated strong and warm solution of ammonia with sulphate of silver, and on cooling prismatic crystals were deposited soluble in water and in aqueous ammonia = $2\text{NH}_3, \text{AgO}, \text{SO}_3$, or perhaps $\text{NH}_3, \text{AgO} + \text{NH}_3, \text{SO}_3$. Potassa throws down fulminating silver from these solutions.

PHOSPHURET OF SILVER may be formed either by projecting phosphorus upon red-hot silver, or by heating a mixture of 1 part of silver filings, 2 of vitrified phosphoric acid, and 0.5 of charcoal. It is a brittle white compound. It loses its phosphorus when fused and exposed to air. Pelletier observed, in regard to this phosphuret, that the fused silver was capable of retaining a larger proportion of phosphorus in combination than after it had solidified; for the fused phosphuret, when it concretes, throws off a quantity of phosphorus, producing a brilliant combustion; there is an analogy between this effect and the similar absorption and evolution of oxygen. The concreted phosphuret consists of 108 silver + 16 phosphorus. According to Landgrebe a phosphuret of silver containing about 33 *per cent.* of phosphorus is formed by fusing 12 parts of tribasic phosphate of silver with 1 part of powdered charcoal at a moderate red-heat.

HYPOPHOSPHITE and PHOSPHITE OF SILVER have not been examined; probably oxide of silver would be reduced by these acids.

PHOSPHATE OF SILVER. $3\text{AgO}, \text{cPO}_5$. When a solution of common phosphate of soda, $2\text{NaO}, \text{HO}, \text{cPO}_5$, is added to nitrate of silver, a yellow anhydrous tribasic phosphate of silver falls, and free nitric acid is found in the supernatant liquor: $3 [\text{AgO}, \text{NO}_5] + \text{NaO}, \text{HO}, \text{cPO}_5 = 3\text{AgO}, \text{cPO}_5 + 2[\text{NaO}, \text{NO}_5] + \text{HO}, \text{NO}_5$. If the solution of nitrate of silver be precipitated with anhydrous tribasic phosphate (subphosphate) of soda $[3\text{NaO}, \text{cPO}_5]$, the supernatant solution remains neutral; in this case $3 [\text{AgO}, \text{NO}_5] + 3 \text{NaO}, \text{cPO}_5 = 3\text{AgO}, \text{cPO}_5 + 3 [\text{NaO}, \text{NO}_5]$. This phosphate fuses at a red-heat. It is soluble in nitric, phosphoric, and acetic acid, and in ammonia and carbonate of ammonia; it is discolored by exposure to light: its specific gravity is 7.3: when heated it becomes brown, but regains its yellow tint as it cools. It consists of

						Berzelius.	Stromeyer.
Oxide of silver	3	348	82.86	82.975
Phosphoric acid	1	72	17.14	17.025
<hr/>							
Tribasic phosphate of silver	1		420		100.00		100.00

When this salt is dissolved in phosphoric acid, a part of it is deposited in granular crystals of the preceding tribasic salt; by spontaneous evaporation of the residuary solution, white plumose crystals are deposited, which, by water, are resolved also into the same salt.

PYROPHOSPHATE OF SILVER, $2\text{AgO},6\text{PO}_5$, is the *white* precipitate thrown down from nitrate of silver by pyrophosphate of soda; in this case the supernatant liquid remains neutral. (CLARK.) $2[\text{AgO},\text{NO}_5] + 2\text{NaO},6\text{PO}_5 = 2\text{AgO},6\text{PO}_5 + 2[\text{NaO},\text{NO}_5]$ Pyrophosphate of silver is anhydrous; its sp. gr. is 5·3; it is fusible at a dull red heat without decomposition; it becomes brownish-red by exposure to light: when boiled with solution of common phosphate of soda, it yields yellow tribasic phosphate of silver, and pyrophosphate of soda. (GMELIN.) It is soluble in cold nitric acid, from which it is precipitated, unchanged, by ammonia; but when boiled in nitric or in dilute sulphuric acid, the pyrophosphoric acid is changed into common phosphoric acid, and then ammonia throws down a yellow precipitate; it is resolved by hydrochloric acid into chloride of silver, and aqueous pyrophosphoric acid; it dissolves in ammonia, and is thrown down again unchanged by acids. It is insoluble in acetic acid, and not altered by boiling in water: its components are

						Berzelius.	Stromeyer.
Oxide of silver	2	232	76·31 76·35 75·39
Pyrophosphoric acid....	1	72	23·69 23·65 24·61
<hr/>							
Pyrophosphate of silver	1		304		100·00	100·00	100·00

METAPHOSPHATE OF SILVER. $\text{AgO},a\text{PO}_5$. This is a white gelatinous precipitate thrown down from solution of nitrate of silver by metaphosphate of soda: boiling water resolves it into an acid and a sesquibasic salt $=3\text{AgO},2a\text{PO}_5$. (BERZELIUS.) The components of the neutral metaphosphate are

						Berzelius.
Oxide of silver	1	116	61·70 64·52
Metaphosphoric acid.....	1	72	38·30 35·48
<hr/>						
Metaphosphate of silver	1		188		100·00	100·00

SELENIURET OF SILVER, AgSe , obtained by precipitating nitrate of silver by seleniuretted hydrogen, is a black powder, which fuses into a globule having a metallic lustre. It consists of 73·16 silver + 26·84 selenium. When silver is fused with selenium, a grey *biseleniuret* is formed, from which excess of selenium is expelled by heat. (BERZELIUS.) Seleniuret of silver occurs native, in combination with about 7 per cent. of seleniuret of lead.

SELENITE OF SILVER, AgO,SeO_2 , is thrown down in the form of a white powder, very sparingly soluble in hot water, on the addition of aqueous selenic acid to solution of nitrate of silver: it is fusible, and at a high heat gives out selenious acid and oxygen, and leaves metallic silver. It is not discolored by exposure to daylight. It may also be obtained by boiling seleniuret of silver in nitric acid: as the solution cools the selenite is deposited in small crystals; or it may be thrown down, by dilution, in the form of a white powder. (BERZELIUS.) *Seleniate of silver* is isomorphous with the sulphate. (MITSCHERLICH.)

CARBURET OF SILVER. When silver is kept in fusion for an hour in contact with lamp-black, it takes up about 3 per cent. of carbon, (GAY LUSSAC. *Ann. Ch. et Ph.*, LViii. 223,) forming Ag_2C . When cuminate

of silver is heated in an open vessel to redness, the residue is a yellow substance, not affected by heat, and soluble in nitric acid, with the exception of 5.5 *per cent.* of carbon: this appears to be AgC . (GERHARDT and CAHOURS.) A carburet of silver also remains when cyanide of silver is intensely heated. When maleate of silver is decomposed by heat, a grey metallic powder remains, containing about 10 *per cent.* of carbon, when purified by solutions of potassa, hydrochloric acid, and ammonia: it is probably AgC_2 . (REGNAULT. *Ann. der Pharm.*, xix. 153.)

CARBONATE OF SILVER, AgO, CO_2 , is precipitated in the form of a pale yellow insoluble powder, by adding carbonate of potassa to nitrate of silver. It blackens by exposure to light, and is easily decomposed by heat. It is readily converted into chloride by hydrochloric acid and soluble chlorides. Moist oxide of silver absorbs carbonic acid from the air. (FISCHER.) Carbonate of silver consists of

						Setterberg.
Oxide of silver	1	116	84.06 84.02
Carbonic acid	1	22	15.94 15.98
<hr/>						<hr/>
Carbonate of silver....	1		138		100.00	100.00

AMMONIO-CARBONATE OF SILVER is thrown down as a white flocculent precipitate when alcohol is added to a solution of carbonate of silver in aqueous ammonia; but when the precipitate is washed with alcohol upon a filter, ammonia is abstracted, and yellow carbonate of silver remains. When alcohol is poured upon the surface of a strong aqueous solution of the ammonio-carbonate, it gradually crystallizes in rhombic tables. As fulminating silver is sometimes formed, this compound must be cautiously treated.

BORATE OF SILVER, AgO, BO_3 , is thrown down from the nitrate of silver in the form of a white crystalline powder, by adding solution of boracic acid. It is very difficultly soluble in water, and easily fusible. The same salt falls on adding a saturated solution of borax to a dilute solution of nitrate of silver: if the borax-solution be very dilute, oxide of silver falls. It consists of

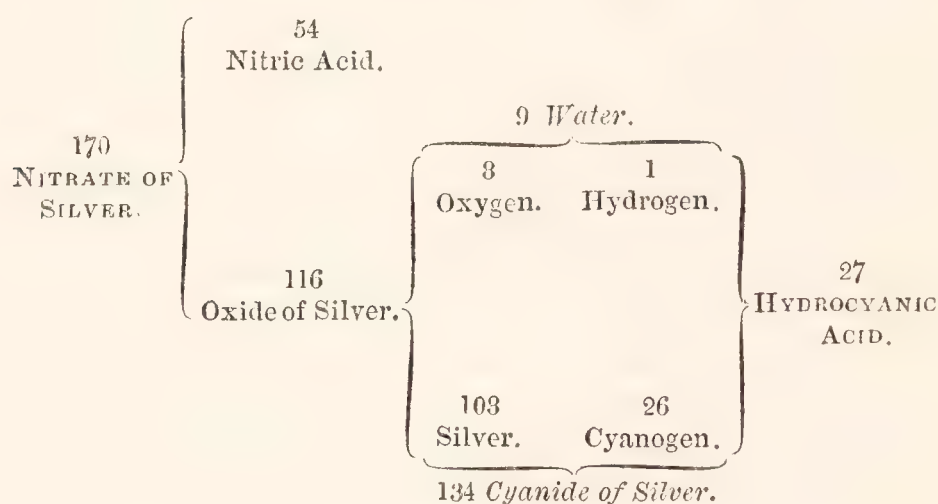
						H. Rose.
Oxide of silver	1	116	76.9 77.1
Boracic acid	1	35	23.1
<hr/>						<hr/>
Borate of silver	1		151		100.0	100.0

CYANIDE OF SILVER. Ag, Cy . Hydrocyanic acid, or solution of cyanide of potassium, causes a white precipitate in solution of nitrate of silver, which is *cyanide of silver*, and which, when heated, fuses, and, at a high temperature, gives out cyanogen. It is insoluble in water and in fixed alkalis, but readily soluble in ammonia. It is soluble, if a little excess of hydrocyanic acid be present, in solution of potassa; (TAYLOR;) this, however, merely amounts to its being soluble in a solution containing cyanide of potassium, and chloride of silver is soluble under the same circumstances. It is decomposed by hydrochloric acid, and by sulphuretted hydrogen; nitric acid scarcely acts upon it, unless concentrated and heated. Sulphuric acid, diluted with its volume of water, decomposes it

when boiling, with the escape of hydrocyanic acid and the formation of sulphate of silver: in this way cyanide may be separated from chloride of silver, which is not affected by sulphuric acid. (GLASSFORD and NAPIER. *Mem. Ch. Soc.*, ii. 93.) It dissolves in a strong solution of nitrate of silver, and forms a compound which may be crystallized, but which is decomposed by solution in water. It is soluble in the alkaline chlorides, in ferrocyanide of potassium, in hyposulphite of soda, and in cyanide of potassium. This cyanide has a place in the Pharmacopœia as an occasional source of hydrocyanic acid: it consists of

Silver	1	108	80·6
Cyanogen	1	26	19·4
<hr/>					
Cyanide of silver	1		134		100·0

The following diagram shows the theory of its decomposition by hydrochloric acid, together with the equivalents of the products:



ARGENTO-CYANIDES. Cyanides of the alkaline bases form soluble double salts with cyanide of silver; they are insoluble in alcohol, which throws them down from their aqueous solutions. The *argento-cyanide of potassium* yields plumose colorless crystals: it produces precipitates in many of the metallic solutions, which are *insoluble argento-cyanides*, corresponding in composition with the ferrocyanides. A solution of oxide or chloride of silver in cyanide of potassium, forms a good liquid for silvering by immersion, especially when aided by electricity: for the solvent, 1 part of cyanide of potassium may be dissolved in 10 of water, and 50 or 60 grains of oxide or chloride of silver dissolved in each pint: the oxide and chloride should both be in a moist state. (See GLASSFORD and NAPIER on these Cyanides. *Mem. Chem. Soc.*, ii. 92.)

FERROCYANIDE OF SILVER falls as a white powder when ferrocyanide of potassium and nitrate of silver are mixed. FERRIDCYANIDE OF SILVER is yellow.

SULPHOCYANIDE OF SILVER falls in the form of a white curdy precipitate when sulphocyanide of potassium is added to nitrate of silver. It slowly blackens by exposure to light. It is insoluble in water, but soluble in strong aqueous ammonia, from which it crystallizes in brilliant white plates.

CYANATE OF SILVER. AgO, CyO . When cyanate of potassa is added to nitrate of silver a white powder falls, somewhat soluble in hot water, and soluble in ammonia, with which it forms a white crystalline compound, but from which the ammonia may be expelled by heat; it blackens when heated, and burns with deflagration, the products being cyanic acid, carbonic acid, nitrogen, and dicyanide of silver. (LIEBIG.) When solution of nitrate of silver is dropped into alcoholic solution of cyanate of potassa, cyanate of silver is also precipitated: subjected to dry distillation, cyanate of silver yields carbonic acid and nitrogen, and the residue forms a paracyanide, evolving at the same time heat and light. (BERZELIUS.)

AMMONIOCYANATE OF SILVER. When a solution of cyanate of silver in ammonia is left to spontaneous evaporation, it deposits translucent lamellar crystals; exposed to air they lose ammonia and become opaque.

FULMINE OF SILVER. ARGENTOFULMINE OF SILVER. FULMINATING SILVER. $2\text{AgO}, \text{Cy}_2\text{O}_2$. This curious and dangerous compound is prepared as follows: 100 grains of fused and finely-powdered nitrate of silver are added to an ounce of warm alcohol, and the mixture stirred in a sufficiently large glass basin; an ounce of fuming nitric acid is then added, and presently a violent effervescence ensues and a powder falls: as soon as this appears white, cold water is added, and the powder is immediately to be collected upon a filter, washed, and carefully dried at a temperature of 100° . In collecting and handling this powder, the utmost caution is requisite; it should be made in small quantities only, and touched with nothing hard, for it has sometimes exploded upon the contact of a glass rod, even under water: the feather of a common quill serves to collect it; and it should be kept in a wide-mouthed vessel covered by paper, and by no means in a stoppered or even a corked phial, as serious accidents have arisen from its unexpected explosion; in short, one cannot be too careful in meddling with it, and its use for fulminating balls and other purposes of amusement is highly dangerous.

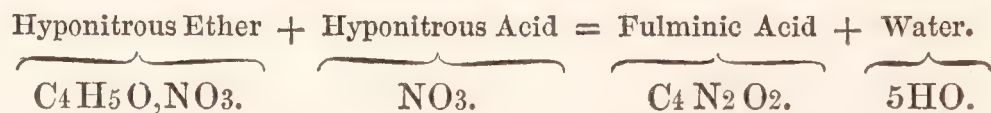
Berzelius observes that, in preparing fulminating silver, a vessel of sufficient capacity should be used to prevent the liquid running over during the effervescence, by which portions of the powder are deposited upon its exterior, and apt to explode when dry; that all approach of flame should be avoided during the escape of the nitrous etherized gas, because its inflammation would probably occasion the powder to explode; and that care should be taken to avoid introducing all hard substances to stir or touch the precipitate.

Liebig's process for the preparation of fulminating silver is as follows: 1 part of standard silver is dissolved in 10 parts of nitric acid of sp. gr. 1.36 to 1.38: the solution is then poured into 20 parts of alcohol (of 85 or 90 *per cent.*), and the mixture gently heated: as soon as it enters into ebullition, the heat is withdrawn, and it is left to itself till cold, when the liquor becomes turbid, and deposits fulminate of silver in the form of brilliant white needles, which, when washed and dried, are equal in weight to that of the metal used. (*Traité de Chim. Org.*, i. 133.) Fownes directs as follows: "Fulminate of silver is prepared by dissolving 40 or 50 grains of silver, which need not be pure, in three-quarters of an ounce by measure of nitric acid, of sp. gr. 1.37, or thereabouts, by the aid

of a little heat; a sixpence answers the purpose very well. To the highly acid solution, while still hot, 2 measured ounces of alcohol are added, and heat applied until reaction commences: the fulminate of silver slowly separates from the hot liquid in the form of small brilliant white crystalline plates, which may be washed with a little cold water, distributed upon separate pieces of filter paper, in portions not exceeding a grain or two each, and left to dry in a warm place. When dry, the papers are folded up and preserved in a box or bottle: this is the only safe method of keeping the salt." (*Manual*, p. 459.)

Fulminating silver is a grey crystalline powder; it acquires a dingy hue by exposure to light; it dissolves in from 30 to 40 parts of boiling water, and as the solution cools, nearly the whole is again deposited in minute crystals. It detonates in the quantity of a grain, or even half a grain, with great violence, when heated, or touched by any hard body; placed upon a piece of rock-crystal, and touched in the slightest manner by another crystal, it explodes violently; upon the contact of sulphuric acid, and by the electric spark, it also detonates.

The nature of this substance has been investigated by Liebig and Gay Lussac (*Ann. Ch. et Ph.*, xxiv. and xxv.), who have shown that it is a compound of 2 atoms of oxide of silver with 1 of fulminic acid: in its formation, a portion of the alcohol is oxidized, so as to form aldehyde, and formic, and oxalic acid; this is effected at the expense of the oxygen of the nitric acid, which passes into hyponitrous acid, and this, reacting upon another portion of the alcohol, forms hyponitrous ether, fulminic acid, and water; 1 atom of hyponitrous ether (hyponitrite of oxide of ethyle) and 1 of hyponitrous acid, containing the elements of 1 atom of fulminic acid and 5 of water.



The bibasic peculiarities of the *fulminates* have been already noticed (p. 508): the components of fulminating silver are

					Gay Lussac and Liebig.				
Oxide of silver	2	232	77·34	77·528	2 232 77·34
Cyanogen	2	52	17·33	17·160	{ Fulminic acid }
Oxygen	2	16	5·33	5·312	
<hr/>									
Fulminate of silver		1		300		100·00		100·000	1 300 100·00

Fulminate of silver is decomposed by hydrochloric acid, with the formation of hydrocyanic acid, water, and chloride of silver, and a compound which has been termed *chlorohydrocyanic acid*, having the formula $\text{C}_2\text{N}, \text{Cl}_5, \text{H}_2$; these results are represented in the following equation (LIEBIG): $2\text{AgO}, \text{C}_4\text{N}_2\text{O}_2 + 7\text{HCl} = \text{C}_2\text{NH} + 4\text{HO} + 2\text{AgCl} + [\text{C}_2\text{NCl}_5\text{H}_2]$. The decomposition of fulminate of silver by zinc and by copper is attended by the same results as when those metals act on fulminating mercury; the silver or mercury are replaced by zinc or copper, and compounds are produced, having the formulæ $2\text{ZnO}, \text{Cy}_2\text{O}_2$, and $2\text{CuO}, \text{Cy}_2\text{O}_2$. (E. DAVY.) The compound regarded by E. Davy as fulminic acid, is $\text{ZnO}, \text{HO}, \text{Cy}_2\text{O}_2$. (FEHLING.)

ARGENTO-FULMINIC ACID. $\text{AgO}, \text{HO}, \text{Cy}_2 \text{O}_2$. This compound is produced by digesting the preceding in solution of potassa, filtering, and adding nitric acid; a precipitate falls, soluble in boiling water, from which crystals separate on cooling, composed of 1 atom of fulminic acid combined with 1 of oxide of silver, and 1 of water: and in which, therefore, in reference to the preceding compound, 1 atom of oxide of silver is replaced by an atom of basic water: these are dangerously explosive. The proximate elements of this compound are

Oxide of silver	1	116	60.41
Water	1	9	4.16
Fulminic acid	1	68	35.43
<hr/>					
Argento-fulminic acid	1		193		100.00

ARGENTO-FULMINATE OF POTASSA. $\text{KO}, \text{AgO}, \text{Cy}_2 \text{O}_2$. When solution of potassa is digested with fulminating silver, half the oxide of silver is thrown down, and, on filtering and carefully evaporating the solution, white foliated crystals may be obtained, of a metallic taste, neutral to tests, soluble in 8 parts of boiling water, and not precipitated by chlorides. They explode by heat and friction. In this, and analogous compounds, therefore, the basic water of the argento-fulminic acid is replaced by the alkaline base, this argento-fulminate consisting of

Potassa	1	...	48	...	20·7	20·7
Oxide of silver.....	1	...	116	...	50·0	{ Argento-fulminic acid. }	79·3
Fulminic acid	1	...	68	...	29·3		
<hr/>							
Argento-fulminate of potassa	1		232		100·0		100·0

ARGENTO-FULMINATE OF SODA, $\text{NaO}, \text{AgO}, \text{Cy}_2 \text{O}_2$, is obtained as the preceding potassa salt; it forms small brown crystals with metallic lustre, and is somewhat more soluble.

ARGENTO-FULMINATE OF BARYTA, $\text{BaO}, \text{AgO}, \text{Cy}_2 \text{O}_2$, forms small grey grains, little soluble in water, and very explosive. The corresponding *strontia salt* has similar properties.

ARGENTO-FULMINATE OF LIME, $\text{CaO}, \text{AgO}, \text{Cy}_2 \text{O}_2$, forms small yellowish heavy crystalline grains, which are difficultly soluble in water.

ARGENTO-FULMINATE OF MAGNESIA, $\text{MgO}, \text{AgO}, \text{Cy}_2 \text{O}_2$, forms strongly explosive capillary crystals: there is also a modification of this salt in the form of a rose-colored inexplusive powder.

CYANURATE OF SILVER. If nitrate of silver be added to cyanurate of potassa, a white precipitate is obtained, which consists of 1 atom of cyanuric acid combined with 2 of oxide of silver and 1 of water. $2\text{AgO}, \text{HO}, \text{Cy}_3 \text{O}_3$. This salt, heated in the dry state, evolves hydrated cyanic acid. If a solution of silver be added to a boiling solution of cyanurate of ammonia, containing ammonia in excess, the cyanurate with 3 atoms of oxide of silver, is formed: $3\text{AgO}, \text{Cy}_3 \text{O}_3$. It is insoluble in water, very sparingly soluble in dilute nitric acid, may be heated to 600° without decomposition, is white, not blackened by light, and at a red-heat emits carbonic acid and nitrogen, and leaves dicyanide of silver. (LIEBIG.) These cyanurates are composed as follows:

Oxide of silver....	2	...	232	...	67.63	...	3	...	348	...	77.33
Water	1	...	9	...	2.63						
Cyanuric acid	1	...	102	...	29.74	...	1	...	102	...	22.67
<hr/>											
Cyanurate A	1		343		100.00		B 1		450		100.00

COBALTO-CYANIDE OF SILVER is a white crystalline precipitate, formed by mixing solutions of cobalto-cyanide of potassium and nitrate of silver. It dissolves in ammonia, with which it forms a double compound, crystallizing in colorless transparent prisms.

ARSENITE OF SILVER, $2\text{AgO}, \text{AsO}_3$, is precipitated in the form of a pale yellow powder, soon becoming deeper yellow, grey, and brown, by the addition of arsenite of potassa, or arsenite of ammonia, to nitrate of silver.

Arsenious acid only produces a white cloud in solution of nitrate of silver, but the yellow arsenite falls on the subsequent addition of a small quantity of alkali. This salt retains its yellow color when carefully dried; it becomes brown on exposure to light: at a red-heat in a glass tube it gives off arsenious acid, and a mixture of arseniate of silver, and metallic silver remains: upon charcoal before the blow-pipe it leaves a globule of silver: it is insoluble in water, but soluble in nitric acid, and in ammonia, when recently precipitated. (MARCET, *Ann. Phil.*, iii. 236.) It is not convertible into arseniate of silver by boiling nitric acid. (LAUGIER, *Journ. de Pharm.*, xi. 487.)

ARSENIATE OF SILVER, $3\text{AgO}, \text{AsO}_5$, is thrown down from nitrate of silver by arsenic acid and by the soluble arseniates, of a reddish-brown color. Before the blow-pipe this compound evolves oxygen and arsenious acid, and arsenical silver remains. Heated in a retort, it fuses, and by the protracted action of a high red-heat, yields metallic silver; it is insoluble in water, but soluble in aqueous ammonia; it dissolves in nitric acid, and in acetic acid: it is an anhydrous tribasic salt, composed of

										Smithson.
Oxide of silver	3	...	348	...	75.16	...	76.69			
Arsenic acid	1	...	115	...	24.84	...	23.31			
<hr/>										
Arseniate of silver	1		463		100.00		100.00			

MOLYBDATE OF SILVER is precipitated in the form of a white powder, insoluble in water. TUNGSTATE OF SILVER is thrown down from nitrate of silver by the alkaline bitungstates, in the form of an anhydrous white powder = $\text{AgO}, 2\text{WO}_3$. (ANTHON.)

CHROMATE OF SILVER, AgO, CrO_3 , is precipitated of a crimson color by mixing solutions of chromate of potassa or soda and nitrate of silver. It soon loses its brilliant tint and becomes brown. It is obtained dark-green and crystalline by boiling bichromate of silver in water, and by exposing an ammoniacal solution of the bichromate, it separates in the form of a dark-green brilliant crust, which becomes red by trituration. It is insoluble in cold, and very little soluble in hot water; it is soluble in ammonia, and in nitric acid: hydrochloric acid decomposes it, and forms chloride of silver: heat resolves it into oxide of chromium and

metallic silver. It forms a double salt with ammonia, and is soluble in solution of chromate of potassa: it consists of

						Warington.
Oxide of silver	1	116	69.05
Chromic acid	1	52	30.95
<hr/>						<hr/>
Chromate of silver		1		168		100.00
						99.33

BICHROMATE OF SILVER. $\text{AgO}, 2\text{CrO}_3$. When a plate of silver is immersed in a mixture of 3 parts of a solution of chromate or of bichromate of potassa with 3 or 4 of oil of vitriol, it becomes covered with red crystals, which are successively formed upon fresh surfaces, the silver being oxidized at the expense of a portion of chromic acid, so that oxide of chromium is formed, yielding at first a brown and then a green solution, which contains chrome-alum. Bichromate of silver is also precipitated by adding bichromate of potassa to an acid solution of nitrate of silver. It forms small plates and prisms, sparingly soluble in water, of a red color, and soluble in nitric acid and in aqueous ammonia: when boiled in water it is resolved into dark-green neutral chromate and an acid solution, which, on cooling, again deposits crystals of bichromate. (WARINGTON. *Phil. Mag. and Journ.*, xi. 489.) Before the blow-pipe, bichromate of silver yields a dark-green bead, and by a continuous white-heat, is resolved into silver and oxide of chromium. Its components are

						Warington.
Oxide of silver	1	116	52.73
Chromic acid	2	104	47.27
<hr/>						<hr/>
Bichromate of silver		1		220		100.00
						99.75

ANTIMONIATE and COLUMBATE OF SILVER are insoluble white powders.

TELLURATE OF SILVER, AgO, TeO_3 , falls as a dark yellow precipitate on mixing concentrated solutions of nitrate of silver and tellurate of potassa: it forms a colorless solution with aqueous ammonia: when boiled in water, it yields a brown sesquibasic salt $= 3\text{AgO}, 2\text{TeO}_3$, and an acid salt remains in solution. When the ammoniacal solution of the above tellurate is mixed with an ammoniacal solution of nitrate of silver and evaporated, it leaves a dark-brown tribasic salt $= 3\text{AgO}, \text{TeO}_3$. This salt is also thrown down on the addition of a solution of bitellurate of potassa, to a very dilute solution of nitrate of silver. (BERZELIUS.)

ALLOYS OF SILVER. The compounds of silver with *potassium*, *sodium*, and other light metals, have not been minutely examined: Davy combined potassium with silver, and formed an alloy which decomposed water; Serullas, by exposing a mixture of silver and tartar to a red-heat, could obtain no alloy. Silver has not been alloyed with *manganese*. It unites difficultly with *iron*: when fused with iron, the alloy separates into silver retaining about one-thirtieth of iron, and iron retaining about one-eightieth of silver; the latter has a peculiar hard and crystalline texture. (MORVEAU, *Journ. de Phys.*, 1788.) When silver and *steel* are fused together, an alloy is formed, which appears perfect while in fusion, but globules of silver exude from it on cooling, which shows the weak attraction of the metals. At a very high temperature, the greater part

by the addition of a small proportion of copper to silver, the metal is rendered harder and more sonorous, while its color is scarcely impaired. Even with equal weights of the two metals, the compound is white: the maximum of hardness is obtained when the copper amounts to one-fifth of the silver. The *standard silver* of this country consists of $11\frac{2}{10}$ pure silver, and $\frac{1}{10}$ copper, or 11.10 silver and 0.90 copper. A pound troy, therefore, is composed of 11 oz. 2 dwts. pure silver, and 18 dwts. of copper. Its density is 10.3; its calculated density is 10.5; so that the metals dilate a little on combining. The French standard for silver coin is constituted of 9 silver and 1 copper. The silver coins of the ancients, and many Oriental silver coins, are nearly pure; they only contain traces of copper and of gold. When silver alloyed by copper, such as standard silver, is exposed to a red-heat in the air, it becomes black from the formation of a superficial film of oxide of copper; this may be removed by immersion in hot diluted sulphuric acid, and a film of pure silver then remains, of a beautiful whiteness: this is called *blanched*, or *dead silver*; the blanks for coin are treated in this way before they are struck, whence the whiteness of new coin, and the darker appearance of the projecting portions occasioned by wear, in consequence of the alloy showing itself beneath the pure surface; articles of plate are often deadened, or *matted*, by boiling in bisulphate of potassa (*sal enixum*), which acts in the same way as the dilute sulphuric acid. When an alloy of silver and copper containing 78 *per cent.* or more of silver is immersed in solution of nitrate of silver, it produces no metallic precipitation: when there is less silver in the alloy, it gradually reduces the silver in the solution, and the rapidity of this effect increases with the preponderance of the copper. (KARSTEN.) Lead and silver form a very brittle dull-colored alloy, from which the lead is easily separated by cupellation (p. 859). When fused lead containing silver is suffered to cool slowly, the lead which first concretes forms granular crystals and is nearly pure, while almost the whole of the silver is contained in the liquid portion; in this way the separation of the two metals may to a certain extent be effected, especially upon the large scale. Antimony forms a brittle white alloy, the density of which exceeds the mean of its components; the greater part of the antimony evaporates during protracted fusion, and the whole may be separated, in the form of oxide, by roasting. There is a rare ore found in Spain, and Suabia, (*antimonial silver*), which has a white metallic lustre, and contains 77 *per cent.* of silver, and 23 of antimony; its density is 9.82: it appears to be Ag_4Sb : another variety from Wolfach, yielded 84 silver and 16 antimony = Ag_6Sb . (KLAPROTH.) Bismuth and silver may be combined by fusion; the alloy is brittle, yellow-white, and lamellar; its density exceeds the mean; the density of an alloy of equal weights of bismuth and silver is 10.7. The alloys with *uranium*, *titanium*, and *cerium*, are not known. The *argentiferous tellurium*, from Nagyag, contains about 62 *per cent.* of silver and 38 of tellurium: it appears therefore to be AgTe . (G. ROSE. *Poggend.*, xviii. 64.) When silver and *arsenic* are fused together, an alloy is formed, composed of 100 silver + 16 arsenic. (GEHLEN.) It is grey, brittle, granular, and by long fusion great part of the arsenic evaporates; it may be entirely got rid of by roasting. Ferro-arsenuret of silver is found *native* at Andreasberg, in the Hartz. (KLAPROTH, *Beitrag*e, i. 187.) 4 parts of silver and 2 of *molybdenum* were strongly

heated, but did not yield a button; by continuing the heat a portion of the silver eliquated, still retaining a part of the molybdenum, and becoming bluish when heated; the residuum being again melted in charcoal became more compact, was brittle, grey, and granular. (THOMSON.) 1 part of silver with 2 of molybdenum forms a grey, granular, brittle alloy. (L. GMELIN.) The alloys of *chromium* and *vanadium* are unknown. 100 parts of silver and 50 of *tungstic acid*, strongly heated with charcoal, gave a brown button, slightly malleable, weighing 142 grains. (THOMSON.) Silver amalgamates easily with *mercury*: when red-hot silver is thrown into heated mercury it dissolves, and when 8 parts of mercury and 1 of silver are thus combined, a granular crystalline soft amalgam is obtained, the density of which exceeds the mean of its components; when a solution of this amalgam in liquid mercury is squeezed through chamois leather, the excess of mercury, retaining only a trace of silver, goes through, and the solid amalgam is left behind. This amalgam exists *native* in octohedral and dodecahedral crystals, varying in composition: a variety from Arqueros, in Chili, contains, according to Domeyto, (*Comptes Rendus*, xiv. 567,) 86·5 *per cent.* of silver, and is = Ag₆Hg; the native amalgam from Moschellandsberg, in the Palatinate, contains about 35 *per cent.* of silver, and appears to be Ag₂Hg; and another variety from Allemont = Ag₃Hg; it contains about 26 *per cent.* of silver. (KLAPROTH, *Beiträge*. CORDIER, *Phil. Mag.*, xiv. 41.) Amalgam of silver is sometimes employed for *plating*; it is applied to the surface of copper, and the mercury being evaporated by heat, the remaining silver is burnished. The better kind of plating, however, is performed by the application of a plate of silver to the surface of the copper, which is afterwards beaten or drawn out. A mixture of chloride of silver, chalk, and pearlash, is employed for silvering brass: the metal is rendered very clean, and the above mixture, moistened with water, rubbed upon its surface. Plating by metallic precipitation from an ammonio-chloride of silver is also frequently resorted to, and electro-plating has now come into very general use, and is likely to supersede the other methods, inasmuch as when the plating is so far worn as to show copper, it can easily be recoated.

ASSAY OF SILVER. The analysis of alloyed silver is a very important process, and in continual practice by refiners and assayers. It may be performed in the humid way by dissolving the alloy in nitric acid, precipitating with hydrochloric acid or chloride of sodium, and either reducing the chloride by potassa in the way above described, or estimating the quantity of silver which it contains. The usual method, however, which is employed at the Mint, and by the refiners, is *cupellation**. Of the useful metals, there are three which are capable of resisting the action of air at high temperatures: these are silver, gold, and platinum; the others,

* Where great accuracy is requisite, the solution of the alloy, and the precipitation of the silver in the state of chloride, is the method that must be followed; but an experienced assayer will arrive at extremely close results by cupellation, and where, as in the London Mint, many assays are often daily requisite, the humid process

could not be adopted without serious interruption to the business of the establishment. Where, as in the French Mint, only one degree of fineness is to be estimated, the humid process, conducted with the *precautions* described by Gay Lussac, and with the aid of his apparatus, is preferable.

under the same circumstances, become oxidized: it might, therefore, be supposed, that an alloy containing one or more of the first three metals, would suffer decomposition by mere exposure to heat and air, and that the oxidizable metal would burn into oxide. This, however, is not the case: for if the proportion of the latter be small, it is protected, as it were, by the former; or, in other cases, a film of infusible oxide coats the fused globule, and prevents the further action of the air. These difficulties are overcome by adding to the alloy some highly-oxidizable metal, the oxide of which is *fusible*. Lead is the metal usually selected for this purpose, though bismuth will also answer. Supposing, therefore, that an *alloy of silver and copper* is to be *assayed*, or analyzed by *cupellation*, the following is the mode of proceeding:—A clean piece of the metal, weighing about 20 grains, is laminated, and accurately weighed in a very sensible balance. It is then wrapped up in the requisite quantity of sheet-lead (*pure*, and reduced from litharge), apportioned by weight to the *quality* of the alloy under examination, and placed upon a small *cupel*, or shallow crucible, made of bone-earth, which has been previously heated. The whole is then placed within the *muffle*, heated to bright-redness: the metals melt, and, by the action of the air which plays over the hot surface, the lead and copper are oxidized and their fused oxides are absorbed by the cupel, and, if the operation has been skilfully conducted, a button of pure silver ultimately remains, the completion of the process being judged of by the cessation of the oxidation and motion upon the surface of the globule, and by the very brilliant appearance assumed by the silver when the oxidation of its alloy ceases. The button of pure metal is then suffered to cool gradually, and its loss of weight will be equivalent to the weight of the alloy which has been separated by oxidation, a certain allowance being made for a small loss of silver, which always occurs, partly by evaporation, and partly carried off with the oxides which are absorbed by the cupel. To perform this process with accuracy, certain precautions are requisite, which can only be learned by practice, so as to enable the operator to gain uniform results. Instructions upon this subject will be found in AIKIN'S *Chemical Dictionary*; in CHILDREN'S *Translation of Thenard on Chemical Analysis*; in VAUQUELIN'S *Manuel de l'Essayeur*; DARCET, GAY LUSSAC, &c.; and in DUMAS' *Chim. app. aux Arts*. (See also LEVOL, *Ann. Ch. et Ph.*, Sept. 1845.)

CHARACTERS OF THE SALTS OF SILVER. The soluble salts of silver are recognised by furnishing a white precipitate with hydrochloric acid, and the soluble chlorides, which blackens by exposure to light, and which is soluble in ammonia; and by affording metallic silver upon the immersion of a plate of copper. The salts insoluble in water are mostly soluble in liquid ammonia, and in nitric acid; when heated on charcoal before the blow-pipe, they afford a globule of silver. All the salts of silver, excepting those which contain colored acids, are colorless, provided they have not been exposed to light, or deoxidizing agents, of the influence of which they are extremely susceptible. A yellow precipitate on the addition of common phosphate of soda and of the soluble arsenites, a red-brown by arseniates, a crimson by the chromates, and white by ferrocyanide of potassium, are further characteristics of the soluble salts of silver.

Tin and lead are the most rapid precipitants of *metallic silver* from the nitrate; cadmium, zinc, copper, bismuth, and antimony, are more slow in their operation, and arsenic and mercury still more tardy. In all cases the silver appears crystallized: often blackish at first, but afterwards assuming the metallic lustre. It is sometimes alloyed with the precipitating metal. Iron is a speedy reducer of the sulphate of silver. The insoluble salts of silver mixed with water are also similarly decomposed, but the operation is more slow. Chromate of silver, probably on account of its insolubility, is extremely slowly reduced; cadmium is the most effective metal for the purpose. Chloride of silver is rapidly reduced by most of the metals which form soluble chlorides, such as zinc, iron, cadmium, cobalt, and arsenic; lead, nickel, copper, antimony, and mercury, act slowly; and tin and bismuth are very feeble in their action. Zinc, copper, and arsenic, rapidly reduce the ammoniacal solution of oxide of silver. Of all the metallic precipitants zinc and cadmium are the most effective; but when zinc or antimony are used, the separated silver contains those metals.

§ XXXII. GOLD. Au. 200.

GOLD has been known from the remotest ages; it is the *Sol* of the alchemists, and they represented it by the circle ☉, which is also the emblem of perfection. Its chemical history has not been so satisfactorily worked out as that of most of the other metals. The best early authority upon it is Lewis (*Philosophical Commerce of the Arts*), and as regards most of its important alloys, Mr. Hatchett's *Experiments and Observations on the Alloys, Specific Gravity, and Comparative Wear of Gold* (*Phil. Trans.*, 1803), must be consulted.

Gold occurs in nature in a metallic state alloyed with silver or copper, and in this state it is called *native gold*. It also occurs in combination with tellurium, and is occasionally disseminated through iron pyrites, which from electrical action is generally passing into oxide of iron. The color of native gold is various shades of yellow; it is either massive, ramose, or crystallized in cubes and octohedra. In these varieties of gold the proportion of silver fluctuates between 8 and 70 *per cent.* (BOUSSINGAULT.) The veins of gold are confined to primitive countries, but large quantities of this metal are collected in alluvial soils, and in the beds of certain rivers, more especially those of the west coast of Africa, and of Peru, Brazil, and Mexico, in America. In Europe, the streams of Hungary and Transylvania have afforded a respectable quantity of gold; it has been found also in the Rhine, the Rhone, and the Danube. In Asia large quantities of gold have been found in the district of the Ural Mountains. Small quantities have been collected in Cornwall, and in the county of Wicklow in Ireland. It is generally found in small nodules and grains, but sometimes it occurs in masses of considerable magnitude, and weighing several pounds: in 1806 one of these was found in the Ural weighing 26 pounds, and in 1842 a similar mass was discovered weighing no less than 83 pounds. Gold is usually separated from the ore or matrix through which it is disseminated, by mechanical division, grinding, and elutriation; and where it is disseminated in

small grains or filaments, mercury is applied, so as to form an amalgam, which is pressed through fine leather to deprive it of excess of mercury, and distilled so as to leave the gold, generally with more or less silver, behind.

Gold may be obtained pure by dissolving standard gold in nitro-hydrochloric acid, (composed of 1 part, by weight, of nitric, and 2 of hydrochloric acid,) evaporating the solution to dryness, (by a gentle heat towards the end of the process,) redissolving the dry mass in distilled water, filtering, acidulating by hydrochloric acid, and adding a solution of protosulphate of iron; a brown powder falls, which after having been washed with dilute hydrochloric acid and distilled water, affords, on fusion with a little borax or other suitable flux, a button of pure gold: for the purpose of solution, gold may conveniently be kept in the pulverulent state, as it originally falls from the acid liquor. If the solution from which the gold is precipitated is extremely dilute, it acquires on the first addition of the salt of iron a beautiful blue tint when viewed by transmitted light, and appears reddish by reflection. The protosulphate of iron is not only a very delicate test of the presence of gold, producing a blue tint in a solution containing not more than a 60,000th part of the metal, but it also throws the whole of it down.

Gold is of a deep and peculiar yellow color. It melts at a bright red-heat, equivalent, according to Daniell, to 2016° of Fahrenheit's scale, and when in fusion appears of a brilliant greenish color: as it solidifies it contracts in bulk, and by very slow cooling was obtained by Tillet and Monge in short quadrangular pyramidal crystals. Its specific gravity, in its least dense state, after fusion, is 19.2; by hammering and rolling it may be brought up to 19.3 or 19.4, or even, according to Berzelius, to 19.65. Its specific heat is $= 0.03244$: (REGNAULT.) 0.0298 (DULONG and PETIT.) It is so malleable, that it may be extended into leaves which do not exceed one two hundred and eighty-two thousandth of an inch in thickness, or a single grain may be extended over 56 square inches of surface. This extensibility of the metal is well illustrated by gilt buttons, 144 of which are well gilt by 5 grains of gold, and less than even half that quantity is adequate to giving them a very thin coating. It is also so ductile that a grain may be drawn out into 500 feet of wire. Reaumur, by rolling out a fine silver-gilt wire, reduced the coating of gold to the 12 millionth of an inch in thickness, and yet under the microscope no imperfection could be perceived in it. According to Fournet, powdered gold admits of being welded into a bar by an operation similar to that by which platinum is forged. (*Ann. Ch. et Ph.*, LXXV. 435.) It may be kept for several hours in fusion in a common furnace without perceptible loss of weight by evaporation; but when subjected to the intense heat of the solar rays condensed upon it by a large and perfect lens, or when submitted to the heat of the voltaic arc of flame, or even to the jet of the oxyhydrogen blow-pipe directed upon charcoal, it affords evidence of volatility. It shows no tendency to unite to oxygen when exposed to its action in a state of fusion; if an electric discharge be passed through a very fine wire of gold, a purple powder is produced, which has been by some considered as an oxide, by others as only finely-divided gold. The pure acids have scarcely any or no action upon pure gold; neither has sulphur or sulphuretted hydrogen; chlorine,

iodine, bromine, and fluorine? on the contrary, are capable of acting upon it; the agent commonly resorted to for dissolving it is chlorine, generally in the form of nitrohydrochloric acid, or *aqua regia*. The combinations of oxide of gold with the alkalis, and the double salts which it forms, are also important features in the history of this metal, and have very extensive and interesting applications to the arts; such solutions are largely used for the purposes of gilding copper and other metals, and have almost entirely superseded the old and pernicious practice of *water-gilding*, as it was termed, in which mercury is used as the solvent.

There is considerable difficulty in determining the equivalent of gold, in consequence of the indefinite character of its protocompounds: hence Gmelin, who originally adopted the number 66 as its equivalent, now employs 199; Graham 99.6; Thomson 100; and Turner 199.2. Following Dr. Turner in the view which he takes of the atomic constitution of the oxides and chlorides of gold, I have assumed 200 as its equivalent, a number not inconsistent with that deduced from its specific heat (p. 62).

PROTOXIDE OF GOLD. AUROUS OXIDE. AuO , is obtained, according to Figuier (*Ann. Ch. et Ph.*, Juillet, 1844), 1. By adding a solution of nitrate of suboxide of mercury to a neutral solution of perchloride of gold, and if necessary boiling the mixture: $\text{AuCl}_3 + 2 [\text{Hg}_2\text{O}, \text{NO}_5] = \text{AuO} + 3\text{HgCl} + \text{HgO}, 2\text{NO}_5$: the nitrate must not be in excess, as in that case calomel would also be formed. 2. Evaporate a solution of perchloride of gold to dryness, and stir the residue till it acquires a yellow color, taking care that the temperature never exceeds 300° ; caustic potassa is then added, and protoxide of gold separates, the liquid becoming deep yellow in consequence of the solution of a part of the oxide in the alkali: if this be filtered, and nitric acid added so as exactly to saturate the potassa, hydrated protoxide of gold falls.

Protoxide of gold is of a dark violet color, appearing almost black when in the state of hydrate: it is not decomposed till heated to above 480° , when it loses oxygen: it is insoluble in water and alcohol: hydrochloric acid converts it into metallic gold and perchloride; this reaction is instantaneous at a boiling temperature: hydriodic acid, in contact with protoxide of gold, acquires a deep yellow color, a yellow-green protiodide of gold is deposited, and the liquid is a solution of the protiodide in hydriodic acid; if boiled, iodine is evolved and gold precipitated: the action of hydrobromic acid resembles that of the hydriodic. Protoxide of gold is soluble in nitrohydrochloric acid; insoluble in nitric, sulphuric, and acetic acids; potassa and soda only dissolve it in its nascent state; with ammonia it forms a purple detonating compound. This oxide has not the instability ascribed to the protoxide of gold by Berzelius; it requires a somewhat higher temperature for its decomposition than the peroxide, and is not affected by light, nor is it affected by alcohol, acetic, or tartaric acid: in its nascent state it is sometimes (not always?) very sparingly soluble in water, giving a violet solution, which, however, deposits its oxide in a few days, or immediately if a soluble salt be added to it. The oxide of gold described by Berzelius as an olive-colored powder of extreme instability, is, according to Figuier, a mixture of protoxide and metallic gold.

Protoxide of gold consists of

						Berzelius.	Figuier.
Gold	1	200	96.15	96.23
Oxygen	1	8	3.85	3.77
<hr/>							
Protoxide of gold	1		208		100.00		100.00

DEUTOXIDE OF GOLD. The existence of this step of oxidizement is very doubtful: it is stated to be the product of the combustion of gold by electricity, as when a powerful electric battery is discharged through a fine wire or leaf of gold: in these cases it is dissipated into a purple powder, which has been called the *purple oxide of gold*, but it is probably either the metal in a state of very minute division, or the protoxide.

PEROXIDE OF GOLD. AURIC OXIDE. AURIC ACID. AuO_3 . According to Pelletier, the best process for obtaining peroxide of gold consists in the decomposition of the *perchloride* by magnesia, washing the precipitate with dilute nitric acid to remove any excess of the precipitant, and drying it at a very low heat. Oberkampf uses potassa for the decomposition of the perchloride, but in that case the oxide is, according to Pelletier, never free from alkali. Wagner suggests the following as the most certain process for procuring peroxide of gold. Dissolve 1 part of gold in nitrohydrochloric acid, render it neutral by evaporation, and redissolve in 12 parts of water; to the solution add 1 part of carbonate of potassa dissolved in twice its weight of water, and digest at about 170° ; carbonic acid gradually escapes, and the hydrated peroxide, of a brownish-red color, subsides; after being well washed, it is dissolved in colorless nitric acid of the specific gravity 1.4, and the solution decomposed by admixture with water; the hydrated peroxide is thus obtained quite pure, and is rendered anhydrous by exposure to a temperature of 212° . (*Turner's Chemistry*.) In this anhydrous state it is nearly black, insoluble in water, and decomposed either by exposure to solar light or by heat. It is soluble in hydrochloric acid, forming the common solution of gold; and it dissolves in sulphuric and in nitric acid, but the affinity is here so weak that the solutions are decomposed by dilution with water, and yield no saline compound when evaporated with the utmost caution. These properties led Pelletier to examine the action of alkalis upon this oxide, and he found that, digested in a solution of caustic potassa, it was dissolved; it also combines with baryta; in these cases it performs the part of a weak acid. Boiled with chloride of potassium or sodium, a yellow solution results, which is alkaline, and contains chloride of gold and aurate of potassa or soda. This oxide consists of

						Berzelius.	Oberkampf.
Gold	1	200	89.3	90.9
Oxygen	3	24	10.7	9.1
<hr/>							
Peroxide of gold	1		224		100.0		100.0

According to Figuier there is a higher oxide of gold, AuO_5 , which he has termed *perauric acid*, formed by boiling auric acid in solution of potassa; a peraurate of potassa and protoxide of gold are the results: $\text{KO} + 2\text{AuO}_3 = \text{AuO} + \text{KO}, \text{AuO}_5$.

PROTOCHLORIDE OF GOLD. AuCl . When perchloride of gold is

placed on a sand-heat in a porcelain capsule, and exposed, under frequent stirring, to the temperature of melting tin, till it no longer evolves chlorine, a pale yellow saline mass remains, which, unless it contains undecomposed perchloride, is not soluble in water: it may be preserved unchanged whilst dry, but in contact of water it gradually changes into perchloride and metallic gold: this decomposition of the protochloride is instantaneous when boiling water is poured upon it, 2 parts of metallic gold being separated for 1 that is held in solution. (BERZELIUS.) It consists of

					Berzelius.	
Gold.....	1	200	84.75 84.9
Chlorine	1	36	15.25 15.1
<hr/>					<hr/>	
Protochloride of gold	1		236		100.00	100.0

PERCHLORIDE OF GOLD. AuCl_3 . When gold in a state of minute division is heated in chlorine, a compound of a deep-yellow color results. Gold-leaf also dissolves easily in a strong aqueous solution of chlorine, and affords a similar compound on evaporation. The common solvent of gold, however, for the purpose of obtaining the chloride, is the nitrohydrochloric acid: $\text{Au} + \text{NO}_5 + 3\text{HCl} = \text{AuCl}_3 + 3\text{HO} + \text{NO}_2$. By evaporation, the saturated solution affords prismatic crystals of a deep orange-color, very deliquescent, fusible, and then decomposed by heat, yielding, at first the protochloride, and ultimately, pure gold. It is said, that, when heated, a very minute portion of the metal also passes off with the chlorine and water. When concentrated sulphuric acid is poured into a strong solution of this compound, it causes a precipitation of *anhydrous chloride of gold*. The color of its aqueous solution varies; if neutral and concentrated it is nearly red (*Leo ruber* of the alchemists); if dilute, or acid, it is yellow. It has a rough bitterish taste, and its effects upon the system resemble those of corrosive sublimate.

The solution of perchloride of gold in hydrochloric acid, (*hydrochlorate of chloride of gold*,) or *muriate of gold*, as it is usually called, yields yellow prismatic or acicular crystals on evaporation; its solution is discolored by steam in the same way, and apparently from the same cause, as nitrate of silver. (See pp. 1017, 1018.) It is decomposed by hydrogen, phosphorus, charcoal, sulphurous acid, and many of the metals; a piece of paper moistened with it and exposed to light, also becomes purple in consequence of its decomposition. According to Van Mons, it is decomposed by several vegetable acids, and when mixed with binoxalate of potassa, carbonic acid gas is evolved, and the gold gradually separated.

The action of perchloride of gold on hyposulphite of soda has been studied by Fordos and Gélis, (*Ann. Ch. et Ph.*, Avril, 1845,) the mixed solution of these salts being used in fixing daguerrotypes, in the proportion of 1 part of perchloride to 3 of hyposulphite, each dissolved in 500 parts of water: the liquid thus resulting is colorless, and contains several salts, but that upon which its photogenic applications depends, appears to be a double hyposulphite of soda and protoxide of gold $= \text{AuO}, \text{S}_2 \text{O}_2, + 3[\text{NaO}, \text{S}_2 \text{O}_2] + 4\text{HO}$; in its formation 8 eq. of hyposulphite of soda, 1 of perchloride of gold, and 4 of water, form 2 of sulphuretted hyposulphate of soda, 1 of the above hydrated double salt, and 3 of chloride of sodium, as in the following equation. $8[\text{NaO}, \text{S}_2 \text{O}_2] + \text{AuCl}_3 + 4\text{HO} = 2[\text{NaO}, \text{S}_4 \text{O}_5] + \text{AuO}, \text{S}_2 \text{O}_2, 3[\text{NaO}, \text{S}_2 \text{O}_2] + 4\text{HO} + 3[\text{NaCl}]$

When solution of protosulphate of iron is added to perchloride of gold, the mixture instantly acquires a dingy brown tinge, and if very dilute, a beautiful green or blue, if viewed by strong transmitted light: these appearances depend upon the presence of an infinite number of small particles of gold in the metallic state; they soon subside in the form of a brown powder, which, after having been washed with boiling water, digested in boiling dilute hydrochloric acid, and again washed and dried, is pure gold; in this pulverulent state, it is used for gilding porcelain, and for some other purposes of the arts; the modes of applying it are described by Dumas. (*Chim. app. aux Arts*, iii. 689.) This method of separating gold from its solution is often convenient in analytical operations, and the gold powder in that case is generally fused into a button with a little borax. According to Dr. Turner, the mutual action of the protosulphate and perchloride is such, that 6 atoms of protosulphate of iron and 1 of perchloride of gold, produce 2 atoms of persulphate of iron, 1 of perchloride of iron, and 1 of gold. $6\text{FeO},\text{SO}_3 + \text{AuCl}_3 = 2[\text{Fe}_2\text{O}_3,3\text{SO}_3] + \text{Fe}_2\text{Cl}_3 + \text{Au}$.

When nitrate or sulphate of silver is added to chloride of gold, a precipitate falls, consisting of chloride of silver and oxide of gold; the latter may be removed by hydrochloric acid: the protosalts of mercury are rendered deep-brown, or reddish brown, by chloride of gold: many organic substances give it a purple hue: it tinges the cuticle of an indelible purple tint: the readiness with which paper and other organic bodies acquire this hue by exposure to light, has led to the use of chloride of gold in some photographic processes.

Perchloride of gold dissolves in alcohol, and in ether: the latter solution is generally obtained by agitating the solution of gold with ether, after which the mixture separates into two portions; the superior is yellow, and is an ethereal solution of chloride of gold; the inferior colorless, being only water and hydrochloric acid. This ethereal solution was formerly much esteemed as a medicine, under the name of *aurum potabile*; it was presumed that gold might possibly communicate something of its own durability to the human constitution. Polished steel dipped into this solution acquires a coat of gold, and it has hence been employed for gilding delicate cutting instruments. It generally slowly deposits films of metallic gold, sometimes in ramose or arborescent crystals. Perchloride of gold consists of

						Berzelius.
Gold	1	200	65 65.09
Chlorine	3	108	35 34.91
<hr/>						<hr/>
Perchloride of gold	1		308		100	100.00

PURPLE OF CASSIUS. This compound was discovered in 1683, by Cassius of Leyden. Protochloride of tin, added to a dilute solution of chloride of gold, occasions an instant change of color to a reddish-brown or dirty purple: if a piece of tin-foil be immersed in a dilute solution of the chloride, the same purple powder is presently thrown down upon it; it is also formed when an alloy of 150 parts of silver, 35 of tin, and 20 of gold, is digested in nitric acid; nitrate of silver is dissolved, and the purple powder remains. According to Graham, the finest-colored precipitate is formed "when protochloride of tin is added to a solution of the perchloride of iron till the color of the liquid has a shade of green, and

adding this liquid, drop by drop, to a solution of perchloride of gold, which is free from nitric acid and very dilute; after 24 hours a brown powder is deposited, which is in a small degree transparent, and purple-red by transmitted light; when dried and rubbed to powder, it is of a dull blue color." (See also DUMAS upon this subject, *Chim. app. aux Arts*, and an abstract of all relating to it by L. GMELIN, *Handbuch*, iii. 687.) The French Pharmacopœia contains the following formula for the purple of Cassius: 10 parts of acid chloride of gold are dissolved in 2000 of distilled water; in another vessel 10 parts of pure tin are dissolved in 10 of nitric and 20 of hydrochloric acid, and the solution diluted with 1000 parts of distilled water. The solution of tin is then added by degrees to that of gold, until no further precipitation ensues: the precipitate is washed, and dried at a gentle heat.

The purple of Cassius is used in enamel and porcelain painting, and also for tinging glass of a fine red color. It retains its color at a high red-heat: it is insoluble in solutions of potassa and soda, but if, whilst in its hydrated state, it be washed with ammonia, a bright purple liquid is obtained, from which the coloring matter very slowly precipitates.

The chemical nature of this compound has given rise to much discussion. It would appear, from Proust's experiments, to consist of about 3 parts of oxide of tin, and 1 of protoxide of gold. Oberkampf found the composition and color of the precipitates formed by protochloride of tin in solution of gold, liable to much variation. When the tin predominates, it is of a violet color; but when the gold is in excess, it is more pink; and these colors are also communicated to enamel. Oberkampf and Macar-dieu assert, that the gold in the compound is in the metallic state; that the violet combination contains 60 oxide of tin and 40 gold, and the pink about 20 and 80 (*Ann. Ch. et Ph.*, xxx. 147); but as mercury does not abstract gold from it, this view is improbable.

According to Berzelius, the purple of Cassius, when heated to redness, loses between 7 and 8 *per cent.* of water, and the residue is a mixture of metallic gold and peroxide of tin. He considers it as a compound of protoxide of gold and sesquioxide of tin. (See also GAY LUSSAC, *Ann. Ch. et Ph.*, xlix.) According to Dr. Turner, the purple of Cassius is a hydrated double salt, composed of peroxide of tin, as the *acid*, united with protoxide of tin and binoxide of gold, as *bases*, in such proportion that the oxygen of the gold exactly suffices to convert the protoxide into peroxide of tin.

Figuier, (*Ann. Ch. et Ph.*, July, 1844,) after reviewing the conflicting opinions respecting the nature of the purple of Cassius, shows that as ordinarily prepared it contains a definite hydrated compound of stannic acid and protoxide of gold, mixed with variable proportions of protoxide of tin, and that this definite compound may be obtained by the action of tin on a solution of gold as follows: Dissolve 20 parts of gold in 100 of aqua regia, consisting of 4 parts of hydrochloric and 1 of nitric acid, and evaporate nearly to dryness: dissolve the residuary chloride of gold in water, filter, and dilute it, (so as to have $\frac{3}{4}$ litre of solution from 20 grammes of gold: or 27 fluid ounces containing about 300 grains of gold,) and put into it small pieces of grain tin; in a few minutes it becomes brown and afterwards purple, and the precipitate may then be collected on a filter, having if necessary previously

heated the liquid and added to it a little common salt, by which an entire precipitation of the purple is insured: in pouring off the liquid holding the purple in suspension, care must be taken to leave the tin behind. The composition of the purple of Cassius so obtained is

						Figuier.
Protoxide of gold	1	208	44.35 44.41
Peroxide of tin....	3	225	47.97 48.61
Water	4	36	7.68 6.98
<hr/>			<hr/>		<hr/>	<hr/>
Purple of Cassius	1		469		100.00	100.00

FULMINATING GOLD. AURATE OF AMMONIA. AMMONIURET OF PEROXIDE OF GOLD. When liquid ammonia is added to a concentrated solution of chloride of gold diluted with about 3 parts of water, a yellowish-brown precipitate is formed, which, if collected upon a filter, washed with a little water, and carefully dried at the temperature of 212° , is *fulminating gold*. 100 grains of gold yield about 125 of product. (BERGMAN.) A more powerfully fulminating compound is obtained by digesting peroxide of gold in liquid ammonia; it acquires a deep olive color, and, after having been well washed, may be dried carefully at 212° . The more carefully this product is washed and dried, the more explosive it becomes, and if long retained at a temperature of about 212° , so as to become perfectly dry, the slightest friction frequently causes it to explode. When suddenly heated to about 290° , it explodes with great violence, and if thus detonated upon platinum leaf, the metal is torn at the point of contact, as is the case with all these explosive combinations: friction with hard bodies, or an electric shock, also explode it. If it be moist it does not explode on the application of heat till dry, and those portions which first become dry explode first; so that in this case it is as it were decomposed by a succession of explosions. The acids and alkalis have little action on fulminating gold. Sulphuretted hydrogen slowly decomposes it, and a solution of protochloride of tin converts it into purple of Cassius. It contains about 77 *per cent.* of gold. It probably consists of 2 atoms of ammonia, and 1 of peroxide of gold, or is a *diaurate of ammonia* $=2\text{NH}_3, \text{AuO}_3$. Dumas regards it as a hydrated nitruret of gold combined with ammonia $=\text{NH}_3, \text{AuN}, 3\text{HO}$: but the former is the more simple and probable view of its proximate composition.

AURO-PERCHLORIDES. Under this term are comprehended the compounds described by Bonsdorff, (*Ann. Ch. et Ph.*, xliv.) Johnston (*Ed. Journ. Science*, iii. 131 and 290,) and others, in which the chloride of gold is combined with certain electro-positive chlorides, such as those of the alkaline bases: they consist of 1 atom of terchloride of gold, and 1 atom of the other chloride, and may be formed of their respective chlorides in such proportions; some of them have been long known: they mostly form prismatic crystals, and include water of crystallization. It is in consequence of the formation of these soluble double salts, that the solution of chloride of gold in hydrochloric acid yields no precipitates with the alkalis, even when added in excess. Different aurochlorides, obtained by adding salts of potassa, soda, ammonia, and other bases, to the chloride, are employed in gilding copper trinkets, buttons, and other articles, under Elkington's patent.

AURO-PERCHLORIDE OF AMMONIUM, $\text{NH}_4\text{Cl}, \text{AuCl}_3, 4\text{HO}$, is formed by dissolving its component salts in atomic equivalents and evaporating; it crystallizes in efflorescent acicular prisms, soluble in water and alcohol, and containing

Chloride of ammonium	1	...	54	...	13·6
Perchloride of gold.....	1	...	308	...	77·4
Water	4	...	36	...	9·0
<hr/>					
Crystallized auro-perchloride of ammonium	1		398		100 0

AURO-PERCHLORIDE OF POTASSIUM. $\text{KCl}, \text{AuCl}_3, 5\text{HO}$. This salt may be obtained by evaporating a mixed solution of chloride of potassium and perchloride of gold, in yellow four-sided prisms, slightly efflorescent, and which, dried at 212° , lose their water of crystallization; at a higher temperature chlorine is evolved, and the salt fuses into a dark-brown liquid, which probably contains protochloride of gold, but which water and dilute hydrochloric acid resolve into the original salt, chloride of potassium and metallic gold being separated, The components of the crystallized double chloride are,

					Johnston.
Chloride of potassium	1	...	76	...	17·8
Perchloride of gold	1	...	308	...	71·7
Water	5	...	45	...	10·5
<hr/>					
Crystallized auro-perchloride of potassium	1		429		100·0
					100·00

AURO-PERCHLORIDE OF SODIUM, $\text{NaCl}, \text{AuCl}_3, 4\text{HO}$, forms four-sided prisms, permanent in the air, and easily fusible in their water of crystallization; they contain

					Johnston.
Chloride of sodium	1	...	60	...	14·85
Perchloride of gold	1	...	308	...	76·24
Water	4	...	36	...	8·91
<hr/>					
Crystallized aurochloride of sodium	1		404		100·00
					100·00

The *auro-perchlorides of lithium, calcium, barium, strontium, magnesium, manganese, zinc, cadmium, cobalt, and nickel* have also been examined by Bonsdorff: they form hydrated prismatic salts, generally similar to the preceding.

PROTIODIDE OF GOLD. AuI . Gold is not acted upon by iodine or hydriodic acid, but when peroxide of gold is digested in aqueous hydriodic acid, protiodide of gold and water are formed, and iodine set free: $\text{AuO}_3 + 3\text{HI} = \text{AuI} + 3\text{HO} + 2\text{I}$. When solution of iodide of potassium is carefully added to a neutral solution of perchloride of gold, protiodide of gold and chloride of potassium are formed, and iodine is also set free: $\text{AuCl}_3 + 3\text{KI} = \text{AuI} + 3\text{KCl} + 2\text{I}$. In these cases the excess of iodine may be expelled by careful heating, and the iodide of potassium must not be added in excess, as it redissolves the iodide of gold. (PELLETIER, *Ann. Ch. et Ph.*, xv.; FORDOS, *Journ. de Pharm.*, xxvii.) Johnston obtains iodide of gold by the action of a solution of iodide of potassium upon protochloride of gold, and dries the washed precipitate in the air. (*Phil. Mag. and Journ.*, ix. 266.) According to

Meillet (*Journ. de Pharm.*, xxvii.; and *Chem. Gaz.*, Jan., 1843), a pure iodide of gold may be obtained by pouring a solution of neutral hydriodate of ammonia into a solution of perchloride of gold as neutral as possible, until no further precipitate ensues: the solutions should be moderately dilute, and about a third of their volume of alcohol should be afterwards added; after some hours the liquor should be decanted from the blackish precipitate, which is a mixture of iodine and iodide of gold, and washed with alcohol, when a semicrystalline iodide of gold remains; it should be dried by exposure to air, and preserved from light: in this way the whole of the gold is precipitated.

Protiodide of gold is a yellow or greenish powder, generally exhibiting more or less of a crystalline aspect; it is nearly tasteless, and insoluble in cold water; when boiled in water it is resolved into its elements; it is not acted upon by cold sulphuric, hydrochloric, or nitric acid, but when heat is applied it is resolved into iodine and gold, a decomposition which takes place slowly at a temperature between 120° and 140° , and rapidly at 250° ; it is immediately decomposed by gaseous (not by aqueous) chlorine, and by solution of potassa. It consists of

						Johnston.	Fordos.
Gold	1	...	200	...	61.35	61.15	61.13
Iodine	1	...	126	...	38.65	38.85	38.87
<hr/>							
Protiodide of gold	1		326		100.00	100.00	100.00

TERIODIDE OF GOLD. AuI_3 . When a solution of terchloride of gold is gradually added to a solution of iodide of potassium, the liquor becomes dark-green, and a dark-green precipitate of teriodide of gold falls, which is again dissolved on agitation. When 1 atom of terchloride of gold has thus been added to 4 atoms of iodide of potassium, the farther addition of the chloride of gold occasions a persistent dark-green precipitate of teriodide of gold, in consequence of the decomposition of the first-formed auroperiodide of potassium: in the first instance, $4\text{KI} + \text{AuCl}_3 = 3\text{KCl} + [\text{KI}, \text{AuI}_3]$; and then, $3[\text{KI}, \text{AuI}_3] + \text{AuCl}_3 = 3\text{KCl} + 4\text{AuI}_3$. (GMELIN.) The precipitated teriodide may be washed without material change, but during drying it loses iodine: exposed at common temperatures to the air it gradually passes into protiodide, and ultimately pure gold remains. Digested in aqueous ammonia it yields a mixture of fulminating gold with iodine. It is decomposed by the alkalis and alkaline earths; it dissolves in aqueous hydriodic acid, and the solution, when subjected to spontaneous evaporation, gradually deposits black crystals, which acquire a purple color on exposure to air. It forms with the more basic iodides a series of *auroperiodides*. (JOHNSTON, *Phil. Mag. and Journ.*, 266.) Its components are

Gold	1	...	200	...	34.6
Iodine	3	...	378	...	65.4
<hr/>					
Teriodide of gold.....	1		578		100.0

AUROPERIODIDE OF AMMONIUM. A solution of hydriodate of ammonia dissolves teriodide of gold and yields black brilliant prismatic crystals, which deliquesce in damp air. (JOHNSTON.)

AUROPERIODIDE OF POTASSIUM. KI, AuI_3 . This salt is formed by adding to a solution of 4 atoms of iodide of potassium nearly 1 atom of terchloride of gold, and leaving the resulting dark liquid to crystallize: $4\text{KI} + \text{AuCl}_3 = 3\text{KCl} + [\text{KI}, \text{AuI}_3]$. The same salt is obtained by dissolving teriodide of gold in a warm solution of iodide of potassium and setting aside to crystallize: it forms brilliant black prisms, which, by exposure to air, gradually lose a portion of iodine; heated in a tube, these crystals leave a prismatic skeleton of gold: they are soluble in hydriodic acid, and in very dilute solution of iodide of potassium; dissolved in water, they sustain partial decomposition. They consist of

						Johnston.
Iodide of potassium	1	166	22.31 22.27
Teriodide of gold	1	578	77.69 77.73
<hr/>						<hr/>
Auroperiodide of potassium	1		744		100.00	100.00

AUROPERIODIDE OF SODIUM. NaI, AuI_3 . The solution of teriodide of gold in iodide of sodium yields brilliant black four-sided prisms, which are very deliquescent. (JOHNSTON.) The *auroperiodides of barium* and of *strontium* have also been described by Johnston.

IODATE OF GOLD. Iodic acid and iodate of potassa form a yellow precipitate in the hydrochloric solution of oxide of gold, which is difficultly soluble in water. (PLEISCHL.)

TERBROMIDE OF GOLD. AuBr_3 . Aqueous bromine dissolves gold, and on evaporation, a dark grey bromide (containing 50 *per cent.* of gold) remains: it may be obtained in dark-red crystals from its aqueous solution: this salt has so intense a color, that it communicates a tinge to 5000 parts of water. (BALARD, *Ann. Ch. et Ph.*, xxxii. 362.) Bromide of gold forms dark-red *aurobromides* with the more basic metallic bromides. (BONSDORFF.)

TERSULPHURET OF GOLD, AuS_3 , is procured by passing sulphuretted hydrogen through an aqueous solution of terchloride of gold. It falls in the form of a black powder, easily resolved by heat into metallic gold and sulphur. (OBERKAMPF, *Ann. de Chim.*, LXXX.) It is also thrown down from the solution of gold by the alkaline hydrosulphurets: when moderately heated in chlorine it yields chloride of sulphur and metallic gold. It consists of

						Oberkampff.	Fellenberg.	Bucholz.
Gold	1	200	80.6 80.39 81.48 82
Sulphur	3	48	19.4 19.61 18.52 18
<hr/>						<hr/>	<hr/>	<hr/>
Tersulphuret of gold	1		248		100.0	100.00	100.00	100

When sulphuretted hydrogen gas is passed through a boiling solution of chloride of gold, the black precipitate which falls is AuS ; it contains about 93 *per cent.* of gold and 7 of sulphur. (BERZELIUS.)

A double *sulphuret of gold and potassium* is formed when sulphuret of gold is digested in a solution of sulphuret of potassium; or when gold, sulphur, and potassa, are fused together; the compound is soluble in water, and acids throw down sulphuret of gold from the solution. This

solubility of gold in alkaline sulphurets was known to the old chemists, and it was thus, according to Stahl, that Moses dissolved the golden calf. This compound is used in the potteries as a source of the preparation of gold with which a dingy gilding is occasionally given to earthenware. (DUMAS.)

No definite *sulphate of gold* has been described, nor has gold been combined with *selenium*.

PHOSPHURET OF GOLD is obtained by heating gold-leaf with phosphorus, in a tube deprived of air. (E. DAVY.) It is a grey substance of a metallic lustre, and consists probably of 1 atom of gold and 1 of phosphorus. It is decomposed when heated under exposure to air. When phosphuretted hydrogen is passed through a dilute solution of chloride of gold, a brown powder falls, which is metallic gold. (H. ROSE.) By the action of great excess of phosphuretted hydrogen, a black phosphuret of gold appears to be produced. (OBERKAMPF.)

PROTOCYANIDE OF GOLD. AuCy , is formed by adding hydrochloric acid to a solution of the potassio-protocyanide of gold and evaporating to dryness; the residue, well washed with water out of direct light, leaves protocyanide of gold in the form of a yellow crystalline powder, tasteless and insoluble in water, alcohol, ether, and acids: boiling solution of potassa deprives it of part of its cyanogen, some gold is reduced, and a double cyanide is formed: sulphuretted hydrogen has no action on it; sulphuret of ammonium dissolves it, and acids throw down sulphuret of gold. It is not affected by light. (See also CARTY, and GLASSFORD and NAPIER, on these cyanides, *Mem. Chem. Soc.*, II. 80.) Cyanide of gold consists of

						Himly.
Gold	1	200	88.5 87.46
Cyanogen	1	26	11.5 12.54
<hr/>						
Protocyanide of gold	1		226		100.0	100.00

AUROPROTOCYANIDE OF AMMONIUM. $\text{NH}_4\text{Cy}, \text{AuCy}$. When saturated solutions of protocyanide of potassium and gold, and of sulphate of ammonia are mixed, and absolute alcohol added, sulphates of ammonia and potassa are precipitated, and the filtered solution yields, on evaporation, crystalline crusts of the ammonio-cyanide of gold, anhydrous, colorless, of a strong metallic taste, soluble in water and alcohol, insoluble in ether, and decomposed between 370° and 480° into cyanide of ammonium and protocyanide of gold. (HIMLY.)

AUROPROTOCYANIDE OF POTASSIUM. POTASSIO-PROTOCYANIDE OF GOLD. KCy, AuCy . Dissolve 7 parts of gold in nitrohydrochloric acid, precipitate with excess of ammonia, wash the precipitated fulminating gold, and put it into a hot aqueous solution of 6 parts of cyanide of potassium: the concentrated solution yields prismatic crystals of the double salt. (HIMLY, *Ann. der Chem. und Pharm.*, xlii., and *Chem. Gaz.*, March, 1843.) This salt is colorless and permanent; its taste sweetish and metallic; it is soluble in 7 of cold, and much less of hot water; slightly soluble in alcohol, and insoluble in ether. Chloride of mercury added to its aqueous

solution throws down protocyanide of gold, and the solution contains chloride of potassium and cyanide of mercury. It consists of

						Himly.
Cyanide of potassium.....	1	66	22.5 22.2
Protocyanide of gold.....	1	226	77.5 77.8
<hr/>						
Auoprotocyanide of potassium	1		292		100.0	100.0

PERCYANIDE OF GOLD. AuCy_3 . According to Liebig, this cyanide is best prepared by adding to a solution of chloride of gold, deprived of free acid, a solution of caustic potassa to which excess of hydrocyanic acid has been added. Excess of cyanide of potassium redissolves the precipitate, but it is again thrown down by an acid. Percyanide of gold is also formed by adding to 16 parts of gold dissolved in nitrohydrochloric acid, a hot solution of 24 parts of cyanide of mercury, evaporating to dryness, and washing with pure water.

Himly recommends precipitating the *auopercyanide of potassium* with nitrate of silver, washing the precipitated cyanide of silver and gold, and adding dilute hydrochloric acid, not in sufficient quantity to decompose the whole: the filtered liquid evaporated in vacuo over sulphuric acid and lime yields a crystalline mass which may be purified by solution in water or alcohol, and then yields colorless tables and prisms of the percyanide, easily soluble in water, alcohol, and ether, fusing at 122° in its water of crystallization, and not reducible by oxalic acid: the formula of the crystals is $\text{AuCy}_3, 6\text{HO}$.

AUOPERCYANIDE OF AMMONIUM, $\text{NH}_4 \text{Cy}, \text{AuCy}_3, 2\text{HO}$, was obtained by saturating a solution of cyanide of ammonium (prepared by distilling ferrocyanide of potassium, sal-ammoniac, and water) with hydrate of oxide of gold, warming the solution, filtering and evaporating to dryness at 212° : the residue was extracted with water, and the aqueous solution left to spontaneous crystallization, gave colorless prismatic crystals, soluble in water and alcohol, scarcely so in ether, becoming opaque at 212° , and afterwards yellow, losing cyanide of ammonium and its products of decomposition, and ultimately leaving gold. (*Chem. Gaz.*, Mar., 1843.)

AUOPERCYANIDE OF POTASSIUM. $\text{KCy}, \text{AuCy}_3$. Convert 35 parts of gold into perchloride as neutral as possible, dissolve in water, and gradually add it to a hot aqueous solution of 46 parts of cyanide of potassium; the liquid becomes colorless and on cooling deposits prismatic crystals which may be purified by recrystallization: exposed to air, they lose water: heated out of contact of air, cyanogen is evolved and the double protocyanide remains. Corrosive sublimate causes no precipitate in the solution of this auopercyanide; protonitrate of mercury a yellow one, when boiled; nitrate of silver a curdy precipitate of cyanide of silver and gold, soluble in ammonia.

Compounds of the cyanide of gold are applied to the purposes of gilding with or without the aid of electricity: for this purpose, the precipitate obtained by adding carbonate of potassa to the perchloride of gold, or the sulphuret of gold obtained by precipitating the perchloride with sulphuret of potassium, are dissolved with heat in a solution of

cyanide of potassium: the proportions may be 1 part of cyanide of potassium to 10 of water; and 50 to 60 grains of the oxide or sulphuret of gold should be dissolved in a pint of such solution. This liquor deposits a perfect film of gold upon many of the metals, by mere immersion, which may in all cases be increased to any required thickness, by electricity. (See p. 220.)

SULPHOCYANIDE OF GOLD is a flesh-colored powder, which falls when solution of sulphocyanide of potassium is mixed with chloride of gold: it is soluble in the precipitant and in ammonia. (GROTHUSS.)

MOLYBDATE OF GOLD. Molybdate of potassa occasions a yellow precipitate in solution of chloride of gold, which is soluble in hydrochloric and in nitric acid. (RICHTER.)

ALLOYS OF GOLD. The alloys of gold with *potassium* and *sodium* have not been examined. With *manganese* it forms a grey brittle alloy, hard, somewhat ductile, and of great lustre: Mr. Bingley found the proportion of manganese to form from one-eighth to one-ninth of the compound: it was obtained by heating gold with oxide of manganese which had been repeatedly mixed and burned with olive oil: cupellation with lead separated the manganese. With *iron* the alloy is malleable and ductile, and harder than gold; its color dull-white, and its specific gravity, when containing 11 gold + 1 iron, 16.885. The metals expand by union; so that, supposing their bulk before combination to have been 1000, after combination it is 1014.7. With *zinc* the compound is brittle and brass-colored: specific gravity, when containing 11 gold + 1 zinc, 16.937. The metals contract a little in uniting; the original bulk being 1000, that of the alloy is 997. The brittleness continued when the zinc was reduced to one-sixtieth of the alloy. The fumes of zinc in a furnace containing fused gold make it brittle. According to Hellot, when an alloy of 1 of gold and 7 of zinc is ignited in an open crucible, the whole of the gold sublimes with the oxide of zinc. *Tin* forms a whitish alloy with gold, which is brittle when thick, but flexible in thin pieces; specific gravity, when constituted of 11 gold + 1 tin, 17.307; bulk before fusion, 1000; after fusion, 981; so that there is considerable contraction. The old chemists called tin, *diabolus metallorum*, from its property of rendering gold brittle; but Bingley's experiments, as quoted by Hatchett, show that one-sixtieth of tin does not render gold brittle; indeed, Alchorne's experiments (*Phil. Trans.*, 1784), showed that gold might be rolled and coined, when containing one thirty-seventh of tin. At a cherry-red heat Bingley found that this alloy became dark-colored, and disintegrated from the loss of the tin. Mercadieu obtained the purple of Cassius by digesting the alloy, rich in tin, in nitric acid: hydrochloric acid dissolves the tin and leaves finely-divided gold. The alloy of gold with *cadmium* has not been examined. Mr. Hatchett obtained a dull-yellow alloy with 11 gold + 1 *cobalt*, the density of which was 17.112. The bulk of the metals before fusion being 1000, became 1001 after fusion. When the cobalt was below one sixty-sixth of the mass, the alloy was somewhat ductile. With gold and *nickel* he obtained a brittle brass-colored alloy, when in the proportions of 11 to 1. The density of the gold being

19.172 and of the nickel 7.8, that of the alloy was 17.068; and the bulk of the metals before fusion being 1000, was increased after fusion to 1007. With *copper*, gold forms a ductile alloy of a deeper color, harder, and more fusible than pure gold: this alloy, in the proportion of 11 gold to 1 copper, constitutes *standard gold*; its density is 17.157, being a little below the mean, so that the metals slightly expand on combining. One troy pound of this alloy is coined into $46\frac{2}{4}\frac{9}{0}$ sovereigns, or 20 troy pounds into 934 sovereigns and a half. The pound was formerly coined into 44 guineas and a half. (See next page.) The standard gold of France consists of 9 parts of gold and 1 of copper. The alloy of gold with *lead* is very brittle when that metal only constitutes one 1920th of the alloy: even the fumes of lead destroy the ductility of gold: the specific gravity of an alloy of 11 gold + 1 lead is 18.080; and 1000 parts become 1005. A remarkable fact in respect to this alloy is, that its specific gravity diminishes to a certain extent, as the proportion of lead diminishes, and is at its maximum when the lead amounts only to one 96th part, the quantity of gold remaining the same, and the deficiency being made up with copper: the following table exhibits this:

Metals.	Grains.	Specific Gravity of Alloy.	Bulk before Union.	Bulk after Union.	Expan- sion.	Metals.	Grains.	Specific Gravity of Alloy.	Bulk before Union.	Bulk after Union.	Expan- sion.
Gold ..	442	18.080	1000	1005	5	Gold ..	442	17.032	1000	1035	35
Lead ..	38					Copper.	34				
						Lead ..	4				
Gold ..	442	17.765	1000	1006	6	Gold ..	442	16.627	1000	1057	57
Copper.	19					Copper.	37.5				
Lead ..	19					Lead ..	0.5				
Gold ..	442	17.312	1000	1022	22	Gold ..	442	17.039	1000	1031	31
Copper.	30					Copper.	37.75				
Lead ..	8					Lead ..	0.25				

Gold and *antimony* form a brittle yellow compound: Hatchett found gold made standard by antimony to be of a pale and dull color, very brittle and fine-grained, and its density 16.929, the bulk of the metals being reduced by combination from 1000 to 987. When the antimony only formed one 1920th of the mass, it was still brittle, and the fumes of antimony in the neighbourhood of fused gold destroy its ductility. A standard alloy of gold with *bismuth* was brittle, fine-grained, and of a greenish-yellow color: its density 18.038: the bulk of the metals being reduced from 1000 to 988. The color of the alloy became nearly that of gold when the bismuth formed one 60th, but it remained brittle with only one 1920th: the fumes of bismuth also destroy the ductility of gold which has been fused in the same furnace. *Uranium*, *titanium*, and *cerium*, have not been examined in their relations to gold. The alloy of gold and *tellurium* exists *native*. *Arsenic* and gold are not easily combined, in consequence of the volatility of the former metal. Hatchett added 453 grains of arsenic to 5307 of fused gold, and having stirred the mixture poured it into an iron mould: only 6 grains were retained, so that the alloy contained one 885th of arsenic; it had the color of gold, and was brittle: by suspending gold in the fumes of arsenic, he obtained a brittle fusible alloy of a grey color. *Molybdenum* and gold form a black brittle compound. (HIELM, *Crell's Annals*, iii.) The action of

TABLE of the Weights, Value, &c., of BRITISH GOLD COIN.

Number of pieces in the pound weight.		Standard weight of each piece.	Fine gold in each piece.	Current weight of each piece not to pass below.	Allowance for the current wear	Remedy by indenture in the lb.		Working remedy for the moneyers, by Mint regulation.			By Mint regulation the Bank must receive, if not heavier than	Legal tender.	Standard weight in troy grains.
						Weight.	Fineness.	On each piece above or below standard.	Heaviest piece.	Lighest piece.			
178	$\frac{1}{4}$ guineas	oz. dwt. gr. 0 1 8.35	oz. dwt. gr. 0 1 5.66	oz. dwt. gr. 0 1 8	gr. .35	gr. 40	gr. 40	gr. .22	oz. dwt. gr. 0 1 8.584	oz. dwt. gr. 0 1 8.134	dwt. gr.		gr. 32.359
133 $\frac{1}{2}$	$\frac{1}{3}$ ditto	0 1 19.14	0 1 15.55	0 1 18	1.14	"	"	.29	0 1 19.445	0 1 18.846			43.146
89	$\frac{1}{2}$ ditto	0 2 16.71	0 2 11.32	0 2 16	.71	"	"	.44	0 2 17.168	0 2 16.269			64.719
44 $\frac{1}{2}$	Guineas	0 5 9.43	0 4 22.65	0 5 8	1.43	"	"	.89	0 5 10.337	0 5 8.539			129.438
22 $\frac{1}{2}$	2 ditto	0 10 18.87	0 9 21.30	0 10 16	2.87	"	"	1.79	0 10 20.674	0 10 17.078			258.876
9, wanting $\frac{1}{2}$ guinea.	5 ditto	1 6 23.19	1 4 17.25	1 6 16	7.19	"	"	4.49	1 7 3.685	1 6 18.697			647.191
93 $\frac{3}{4}$ or 1869 in 20 lbs.	$\frac{1}{2}$ sovereigns.	0 2 13.63	0 2 8.500	0 2 13.125	$\frac{1}{2}$ = .512	12	15	.128	0 2 13.765	0 2 13.508	2 13 { 803 = $\frac{1}{6}$ gr. ab. Stan.		61.163
46 $\frac{2}{3}$ or 934 $\frac{1}{2}$ in 20 lbs.	Sovereigns.	0 5 3.27	0 4 17.001	0 5 2.5	$\frac{3}{4}$ = .774	"	"	.256	0 5 3.531	0 5 3.017	5 3 { 607 = $\frac{1}{3}$ gr. ab. Stan.		123.274
23 $\frac{1}{4}$ and $\frac{9}{16}$	£2 pieces.	0 10 6.54	0 9 10.003	0 10 5	1.548	"	"	.513	0 10 7.062	0 10 6.035			246.548
9 and $\frac{6}{10}$	£5 pieces.	1 5 16.37	1 3 13.008	"	"	"	"	1.284	1 5 17.656	1 5 15.088			616.372

The assays of gold are reported in carats and grains; the lowest is $\frac{1}{18}$ ct. gn. = 7 $\frac{1}{2}$ troy grains.
Deliveries of coin are made in journey-weights, each journey = 15 lbs. troy, in value £700 17s. 6d.

gold and *chromium* has not been examined. Little is known of the compound of gold with *tungsten*: "When 100 parts of gold, 50 of tungstic acid, and a quantity of charcoal-powder, were strongly heated in a covered crucible, complete fusion did not take place; the button weighed 139 grains; by cupellation with lead the gold was reduced to its original purity." *Mercury* and gold combine readily at common temperatures, and more rapidly when heated, the mercury taking up a considerable proportion of gold without loss of fluidity: when rich in gold, the amalgam is of a buttery consistence, and may be separated from the more liquid portion by pressure through leather; it then consists of about 2 parts of gold and 1 of mercury: the amalgam used for gilding bronze contains about one-eighth of gold. *Silver* and gold appear to combine readily in all proportions, when the fused metals are stirred together; but that there is a tendency to definite combination appears from Homberg's experiments, who kept equal parts of gold and silver in fusion for a quarter of an hour, and found on breaking the crucible that the ingot consisted of two distinct portions; the uppermost being pure silver, and the lowermost, gold, combined with one-sixth of silver: the density of this alloy is a little below the mean, and the color of gold is rendered paler by a twentieth part of silver. The standard gold which is at present coined is for the most part alloyed with copper only; previous to the year 1826, the alloy always consisted in part of silver, hence the paler color of the sovereigns and half sovereigns of former coinages: an alloy composed of equal parts of silver and copper furnishes the best addition to gold for the purpose of coinage, and it is to be regretted that this requisite portion of silver is not made part of the *value* of the coin, by which the system of melting our gold coin for the purpose of extracting its silver would be prevented, and the perfection and facility of coinage ensured. To separate the silver from gold, the alloy is melted with great excess of silver, granulated, and boiled in sulphuric acid, by which the silver is oxidized and converted into sulphate of silver, and the metallic gold remains in the form of an insoluble black powder, which is afterwards collected, washed, and fused into a button or ingot. In the same way, the small quantity of gold contained in silver coin, which used to pass unheeded, is extracted by sulphuric acid; the recently coined silver will accordingly be found, in most cases, destitute of those traces of gold which are contained in our coin of a date anterior to 1826, and in Spanish dollars and much other foreign silver. When gold and silver are parted by the action of nitric acid, it is necessary, as in the case of sulphuric acid, that the silver should be in great excess; it is otherwise partially protected from the solvent power of the acid. Not only are small portions of silver volatilized, or in some way carried off by the nitrous vapor, but gold may also be detected in the condensed fumes. In parting furnaces, the nitrous fumes are sometimes carried downwards so as to pass through the fire, and in these cases traces of the precious metals are found in the cinders or ashes. (JOHNSON.)

ASSAY OF GOLD. The analysis of most of the alloys of gold is performed by cupellation. A triple alloy of gold, silver, and copper, provided there be a sufficiency of silver present, may be analyzed by digesting it in nitric acid, which takes up the silver and copper, and leaves the gold

in the form of a black powder, which may be fused into a button; the silver may be thrown down in the state of chloride by solution of common salt, and the copper precipitated by iron, or it may be thrown down and weighed as oxide. The *assay of gold* is more complicated than that of silver, in consequence of the double operation which it has to undergo, namely, first cupellation, and then the separation of the silver from the gold by the action of nitric acid. The real quantity of gold or silver taken for an assay is very small; whatever it may be, it is called the *assay pound*. The silver assay pound is divided into 12 ounces, and each ounce into penny-weights and half penny-weights. The gold assay pound is subdivided into 24 carats, and each carat into 4 carat grains, quarters, and eighths. (AIKIN'S *Dictionary*, Art. ASSAY. See also the authorities above quoted, under the Assay of Silver.)

CHARACTERS OF THE SALTS OF GOLD. It will be observed from the preceding account, that there are, strictly speaking, very few crystallizable or definite oxysalts of gold, but that it forms haloid combinations, which are easily decomposed and reduced by heat; such of these as are soluble, are recognised by the peculiar precipitates which they afford with protochloride or sesquichloride of tin, and with protosulphate of iron, and by a black precipitate with nitrate of suboxide of mercury. The facility of their decomposition by some other reducing agents is also very remarkable; thus phosphorous, and hypophosphorous and phosphorous acids, sulphurous acid and the sulphites, nitrous acid and nitric oxide gas, all throw down metallic gold from the solution of its chloride. Some organic salts and acids also produce characteristic effects upon the solution of chloride of gold, and amongst them the meconic acid, as was first observed by Cooper, occasions a black or purple color in extremely dilute solutions of gold: this test is often of use in recognising the presence of opium: a single drop of tincture of opium in 8 ounces of water is sufficient to occasion a discoloration on the addition of a drop or two of a solution of chloride of gold. Gold is precipitated in the metallic state from its chloride, or hydrochloric solution, by the greater number of the metals: iron, copper, zinc, and tin, rapidly effect this reduction; lead, mercury, and antimony, more slowly; the tardiness of action is sometimes caused by the adhesion of a film of gold to the precipitating metal. When silver is used, the production of its chloride also impedes the effect: and the same happens with palladium. The gold is generally separated in the form of a brown powder; but copper, iron, zinc, and cadmium, occasion the appearance of a bright film: and bismuth, antimony, arsenic, and palladium, become coated with a brilliant covering. Tin, after the separation of a part of the gold, forms the purple of Cassius. The color and perfection of the metallic precipitation of gold is much influenced by the nature and state of dilution of the salt from which it is precipitated, and where electro-chemical depositions are resorted to, the electrical power employed, as well as the nature and temperature of the auriferous liquor, require careful attention and management, in order to ensure a uniform, brilliant, and adhering coating. The other distinctive characters of the salts of gold will be obvious from the preceding details.

§ XXXIII. PLATINUM. Pt. 99.

THIS metal was first made known in Europe by Mr. Charles Wood, who met with its ore in the West Indies, in 1741, and sent specimens of it to Dr. Brownrigg, which he afterwards presented to the Royal Society. In 1750, a paper was published upon it by Mr. Wood (*Phil. Trans.*), and by Dr. Lewis, in 1754. In 1752 a dissertation upon it was published by Scheffer, of Sweden; and in 1757 by Margraaf. (*Mém. Berlin.*) The labors of later experimentalists in reference to this metal, I shall presently have occasion to quote. Its name is a diminutive of the Spanish word *plata*, silver.

Platinum is found in the metallic state, in small grains, in South America, confined to streams and to alluvial strata, chiefly in Brazil and Peru. It has also been found in the province of Antioquia, in North America; and in considerable quantities in the Uralian mountains of Siberia. (*Edin. Quart. Jour. of Science*, v. 323.) The grains, besides platinum, contain generally gold, iron, lead, palladium, rhodium, iridium, and osmium, and often oxide of titanium and chromate of iron. Rounded masses of the metal, however, occasionally occur among them, and are met with in mineral collections; these are rarely larger than a pea or a small marble, though some have been found of the size of a pigeon's egg and upwards. In 1827 a mass of this metal weighing somewhat more than 9½ pounds avoirdupois, was found in the Ural; its sp. gr. was 16. (*Poggend.*, x. 487.) Boussingault has discovered veins of platinum in the sienitic rocks of Santa Rosa, in the province of Antioquia. (*Ann. de Ch. et. Ph.*, xxxii.) Traces of platinum have also been detected in the auriferous sand of the Rhine, and in the gold of Wilhelmshütte in the Hartz.

The following analyses of the ore of platinum from five different localities are given by Berzelius. (*Lehrbuch.*)

	Nischne-Tagilsk, in Siberia.		Gorobla- goldat, in Siberia.	Barbacoas, Antioquia, S. America.	Choco, S. America.	Pinto, S. America.
	Not magnetic.	Magnetic.				
Platinum	78·94	53·58	86·50	84·30	86·16	84·34
Iridium	4·97	2·35	1·46	1·09	2·58
Rhodium	0·86	1·15	1·15	3·46	2·16	3·13
Osmium	1·03	0·97	0·19
Palladium	0·28	0·30	1·10	1·06	0·35	1·66
Iron	11·04	12·98	8·32	5·31	8·03	7·52
Copper	0·70	5·20	0·74	0·40
Osmic-iridium, and other sub- stances }	1·96	2·30	1·40	0·72	2·01	1·87
	98·75	97·86	98·92	98·08	101·17	101·29

The following details respecting the mode of purifying crude platinum, and rendering it malleable, are taken from Dr. Wollaston's latest paper upon this subject published in the *Philosophical Transactions* for 1829*.

“The usual methods of giving chemical purity to this metal, by solution in aqua regia and precipitation with sal-ammoniac, are known to every chemist; but I doubt whether sufficient care is usually taken to avoid dissolving the iridium contained in the ore, by due dilution of the solvent. In an account which I gave in the *Philosophical Transactions* for 1804, of a new metal, Rhodium, contained in crude platinum, I have mentioned this precaution, but omitted to state to what degree the acids should be diluted. I now, therefore, recommend, that to every measure of the strongest muriatic acid employed, there be added an equal measure of water; and, that the nitric acid used be what is called ‘single aqua-fortis;’ as well for the sake of obtaining a purer result, as of economy in the purchase of nitric acid. With regard to the proportions in which the acids are to be used, I may say, in round numbers, that muriatic acid, equivalent to 150 marble, together with nitric acid equivalent to 40 marble, will take 100 of crude platinum; but in order to avoid waste, and render the solution purer, there should be in the menstruum a redundancy of 20 *per cent.* at least of the ore. The acids should be allowed to digest three or four days, with a heat gradually raised. The solution, being then poured off, should stand until a quantity of fine pulverulent ore of iridium, suspended in the liquid, has subsided; and should then be mixed with 41 parts of sal-ammoniac, dissolved in about five times their weight of water. The first precipitate, which will thus be obtained, will weigh about 165 parts, and will yield about 66 parts of pure platinum. As the mother-liquor will still contain about 11 parts of platinum, these, with some of the other metals yet held in solution, are to be recovered by precipitation from the liquor with clean bars of iron, and the precipitate is to be redissolved in a proportionate quantity of aqua regia, similar in its composition to that above directed: but in this case, before adding sal-ammoniac, about 1 part by measure of strong muriatic acid should be mixed with 32 parts by measure of the nitromuriatic solution, to prevent any precipitation of palladium or lead along with the ammoniomuriate of platinum. The yellow precipitate must be well washed, in order to free it from the various impurities which are known to be contained in the complicated ore in question; and must ultimately be well pressed, in order to remove the last remnant of the washings. It is next to be heated, with the utmost caution, in a black-lead pot, with so low a heat as just to expel the whole of the sal-ammoniac, and to occasion the particles of platinum to cohere as little as possible; for on this depends the ultimate ductility of the product.

“The grey product of the platinum, when turned out of the crucible, if prepared with due caution, will be found lightly coherent, and must then be rubbed between the hands of the operator, in order to procure, by the gentlest means, as much as can possibly be so obtained of metallic powder, so fine as to pass through a fine lawn sieve. The coarser parts

* See Gmelin's *Handbuch der Chemie* (Edit. 1844) for a valuable abstract of the several methods of treating the ore of platinum for the separation of the metal.

are then to be ground in a wooden bowl with a wooden pestle, but on no account with any harder material capable of burnishing the particles of platinum; since every degree of burnishing will prevent the particles from cohering in the further stages of the process. Since the whole will require to be well washed in clean water, the operator, in the later stages of grinding, will find his work facilitated by the addition of water, in order to remove the finer portions as soon as they are sufficiently reduced to be suspended in it.

“Those who would view this subject scientifically should here consider, that as platinum cannot be fused by the utmost heat of our furnaces, and consequently cannot be freed, like other metals, from its impurities, during igneous fusion, by fluxes, nor be rendered homogeneous by liquifaction, the mechanical diffusion through water should here be made to answer, as far as may be, the purposes of melting; in allowing earthy matters to come to the surface by their superior lightness, and in making the solvent powers of water effect, as far as possible, the purifying powers of borax and other fluxes in removing soluble oxides.

“By repeated washing, shaking, and decanting, the finer parts of the grey powder of platinum may be obtained as pure as other metals are rendered by the various processes of ordinary metallurgy; and, if now poured over, and allowed to subside in a clean basin, a uniform mud or pulp will be obtained, ready for the further process of casting.

“The mould which I have used for casting is a brass barrel $6\frac{3}{4}$ inches long, turned rather taper within, with a view to facilitate the extraction of the ingot to be formed, being 1.12 inches in diameter at top, and 1.23 inches at a quarter of an inch from the bottom, and plugged at its larger extremity with a stopper of steel, that enters the barrel to the depth of a quarter of an inch. The inside of the mould being now well greased with a little lard, and the stopper being fitted tight into the barrel by surrounding it with blotting-paper, (for the paper facilitates the extraction of the stopper, and allows the escape of water during compression,) the barrel is to be set upright in a jug of water, and is itself to be filled with that fluid. It is next to be filled quite full with the mud of platinum; which, subsiding to the bottom of the water, is sure to fill the barrel without cavities, and with uniformity, a uniformity to be rendered perfect by subsequent pressure. In order, however, to guard effectually against cavities, the barrel may be weighed after filling it, and the actual weight of its contents being thus ascertained, may be compared with that weight of platinum and water which it is known by estimate that the barrel ought to contain. A circular piece of soft paper first, and then of woollen cloth, being laid upon the surface, allow the water to pass, during partial compression by the force of the hand with a wooden plug. A circular plate of copper is then placed upon the top, and thus sufficient consistency is given to the contents to allow of the barrel being laid horizontally in a forcible press.

“The press which I have generally used for this purpose consists of a flat iron bar AB, set edgeways, and screwed down by a hook E, near its middle, where it would otherwise be liable to bend, to a strong wooden bench CD. The bar is connected by a pivot at its extremity A, with the lever AFG. An iron rod FH, which turns at its two extremities upon the pivots F and H, proceeds from the lever at F, and, as the lever

cake. To prevent the blistering of the platinum by heat, which is the usual defect of this metal in its manufactured state, it is essential to expose the cake to the most intense heat that a wind-furnace can be made to receive, more intense than the platinum can well be required to bear under any subsequent treatment; so that all impurities may be totally driven off, which any lower temperature might otherwise render volatile. The furnace is to be fed with Staffordshire coke, and the action of the fire is to be continued for about twenty minutes from the time of lighting it, a breathing heat being maintained during the last four or five minutes. The cake is now to be removed from the furnace, and being placed upright upon an anvil, is to be struck, while hot, on the top, with a heavy hammer, so as at one heating effectually to close the metal. If in this process of forging the cylinder should become bent, it should on no account be hammered on the side, by which treatment it would be cracked irremediably; but must be straightened by blows upon the extremities, dexterously directed, so as to reduce to a straight line the parts which project.

“The work of the operator is now so far complete, that the ingot of platinum may be reduced, by the process of heating and forging, like that of any other metal, to any form that may be required. After forging, the ingot is to be cleaned from the ferruginous scales which its surface is apt to contract in the fire, by smearing over its surface with a moistened mixture of equal parts by measure of crystallized borax and common salt of tartar, which, when in fusion, is a ready solvent of such impurities, and then exposing it, upon a platinum-tray, under an inverted pot, to the heat of a wind-furnace*. The ingot, on being taken out of the furnace, is immediately to be plunged into dilute sulphuric acid, which in the course of a few hours will entirely dissolve the flux adhering to the surface. The ingot may then be flattened into leaf, drawn into wire, or submitted to any of the processes of which the most ductile metals are capable.

“The perfection of the methods above described, for giving to platinum complete malleability, will best be estimated by comparing the metal thus obtained, in respect of its specific gravity, with platinum which has undergone complete fusion; and by comparing it, in respect of its tenacity, with other metals possessing that quality in the greatest perfection. The specific gravity of platinum, drawn into fine wire, from a button which had been completely fused by the late Dr. E. D. Clarke, with an oxy-hydrogen blow-pipe, I found to be 21.16. The aggregate specific gravity of the cake of metallic mud, when first introduced into the barrel, exclusively of moisture, is about 4.3; when taken from the press it is about 10. That of the cake fully contracted, on being taken out of the wind-furnace before forging, is from 17 to 17.7. The mean specific gravity of

* “The chemist will find this flux very serviceable for removing from his crucible or other vessels of platinum those ferruginous scales with which, after long use, and particularly after being strongly heated in a coal or coke fire, they become incrustated. In the analysis of earthy minerals, I have been in the habit of using a similar flux, composed of two parts by weight of crystallized carbonate of soda,

and one of crystallized borax, well ground together. It has the advantage of not acting, like caustic alkali, upon the platinum crucible, and is a powerful solvent of jargon and many other minerals, which yield with difficulty to other fluxes. If the mineral to be operated on requires oxidation, in order to decompose it, a little nitre or nitrate of soda may be added.”

the platinum, after forging, is about 21·25, although that of some rods, after being drawn, is 21·4; but that of fine platinum wire, determined by comparing the weight of a given length of it with the weight of an equal length of gold wire drawn through the same hole, I find it to be 21·5, which is the maximum specific gravity that we can well expect to be given to platinum.

“The mean tenacity, determined by the weights required to break them, of two fine platinum-wires, the one of $\frac{1}{3000}$, the other of $\frac{1}{3850}$ of an inch in diameter, reduced to the standard of a wire $\frac{1}{10}$ of an inch in diameter, I found to be 409 pounds; and the mean tenacity of eleven wires, beginning with $\frac{1}{4500}$ and ending with $\frac{1}{25000}$ of an inch, reduced to the former standard, I found to be 589 pounds; the maximum of these eleven cases being 645 pounds, and the minimum 480 pounds. The coarsest and the finest wire which I tried present exceptions, since a wire of $\frac{1}{150}$ of an inch gave 290 pounds, and a wire of $\frac{1}{30000}$ of an inch, 190 pounds. If we take 590 pounds, as determined by the eleven consecutive trials, to be the measure of the tenacity of the platinum prepared by the process above described, and consider that the tenacity of gold-wire, reduced to the same standard, is about 500, and that of iron-wire 600, we shall have full reason to be satisfied with the processes above detailed, by which platinum has been rendered malleable*.”

The specific heat of platinum, as determined by Dulong and Petit, is 0·0314, and by Regnault, 0·03243. While, therefore, the atomic weight of platinum is the same as that of iridium, its specific heat is sensibly different, (that of iridium 0·03683,) but this probably arises from mechanical causes, as iridium cannot be obtained by artificial means of the same density as when native. (BERZELIUS.) Its color is between that of iron and silver. When pure and free from iridium, it scarcely yields in malleability to gold and silver, and it is excessively ductile, and takes a good polish. In its ordinary state it retains a little iridium, and admits of drawing into wire of 1-1940th of an inch diameter, and is harder than copper, but softer than iron. According to Berzelius, the presence of a little iridium improves the strength and useful qualities of platinum. According to Wollaston, the tenacity of platinum, as already stated, closely approaches that of iron. The specific gravity of pure platinum exceeds that of all other substances, fluctuating between 21 and 22. Berzelius gives it as = 21·45, Wollaston 21·53, and Klaproth, 21·74. Its extreme difficulty of fusion, and the perfect manner in which it resists the action of almost all acids, at a boiling or even at a red-heat, render it importantly useful in many of the arts, and indispensable for various purposes in the chemical laboratory; in short, in these respects, it unites the valuable properties of gold with those of porcelain. The curious catalytic action of *clean surfaces* of platinum, and of *pulverulent* and *spongy platinum*, and *black platinum* upon gaseous mixtures, and especially in determining the combination of oxygen and hydrogen, has also rendered it useful in gaseous analyses, and seems likely to lead to other applications. A piece of paper, dipped into solution of chloride of platinum, dried and burned, yields an ash which exhibits the properties of

* The method followed in Paris for obtaining pure platinum is described by Baruel. (*Quart. Journ. Science*, xii.)

finely-divided platinum in perfection. This *catalytic* action of platinum appears increased in proportion to the mechanical division of the metal and the perfect cleanliness of its surface.

Catalytic platinum may be prepared in several ways. (1.) By fusing together 1 part of platinum and 2 of zinc, and acting upon the alloy by dilute sulphuric acid; then boiling the residuary pulverulent platinum first in nitric acid, then in a solution of caustic potassa, and lastly in distilled water: when dry it is a dark-grey powder, without metallic lustre. (2.) Ammonio-chloride, or potassio-chloride of potassium, is mixed with dilute hydrochloric acid, and pure zinc put into the mixture; the platinum is reduced, and must be digested in warm nitric acid, or dilute sulphuric acid, to remove adhering zinc. (BÖTTGER, *Ann. der Pharm.*, xxxvii. 116.) (3.) Protochloride of platinum is dissolved in a strong warm solution of caustic potassa, and alcohol added whilst the mixture is stirred, till the effervescence, arising from the escape of carbonic acid, ceases, and which is so violent as to require the use of a capacious vessel: the platinum falls in the form of a black powder, from which the supernatant liquor is poured off: the powder is then boiled successively in alcohol, in hydrochloric acid, and in solution of potassa, and lastly in four or five portions of distilled water. If the alcohol were not entirely removed, the powder would ignite on drying, and lose its catalytic power. When dry, it looks like lamp-black, but acquires a metallic aspect after having been heated white-hot. (LIEBIG.)

Catalytic platinum absorbs gases (in the same way as charcoal?) and, without combining with it, they become condensed in its pores: it thus absorbs from 30 to 40 volumes of ammonia, and whilst thus saturated, its catalytic power is destroyed. Liebig's platinum black, when exposed to air, absorbs oxygen only, to the extent of 250 times its volume. It induces various combinations: its action on mixtures of oxygen and hydrogen, and its applications to eudiometrical purposes, &c., have already been elsewhere noticed, as also its power of inducing a variety of other combinations and decompositions. (p. 304.)

Although platinum is infusible in the highest heat of a furnace, it softens so as to admit of welding and forging, as above stated; but in the arc of flame of the voltaic current, and before the oxyhydrogen blow-pipe, it admits of being fused even in considerable masses, and when very intensely heated it boils and evaporates, and thin filaments of it scintillate and appear to burn. Dumas states that when platinum is fused in contact with common charcoal, it becomes harsh and brittle by combination with a little silicium.

Although pure platinum is insoluble in nitric acid, yet when adequately alloyed with certain other metals soluble in that acid, it is taken up; as for instance, with silver. It is attacked at high temperatures by the alkalis, especially by lithia and potassa, and also by nitre and the alkaline persulphurets: it is not affected by sulphur unless in the spongy or finely-divided state, but it combines with the greater number of the metals, and with many of them forms very fusible compounds; these actions will be presently particularly considered; they show the necessity of caution as to the substances which are ignited or fused in platinum crucibles, and as to the fuel with which they are brought into contact.

The determination of the equivalent of platinum is open to the same

difficulties as that of gold. I have adopted 99, which will be found sufficiently consistent with the analytical results which I shall quote. Turner, upon the authority of Berzelius, assumes 98·8, and L. Gmelin, who formerly adopted the lower equivalent, 48, now uses 99. The number 99 nearly agrees with the deduction from its specific heat (p. 62).

PLATINUM AND OXYGEN. The affinity of this metal for oxygen is like that of gold extremely feeble; it shows no disposition to become an oxide, by exposure to air or oxygen at any temperature; and although a strong electric discharge, when transmitted through a fine platinum-wire, dissipates it into black dust, this, as in the analogous case of gold, is probably finely-divided metal, and not the result of combustion or oxidizement. Four definite oxides of platinum are supposed to exist, but of these only two can be satisfactorily identified.

PROTOXIDE OF PLATINUM. PtO . When protochloride of platinum is gently heated in a solution of caustic potassa, a black oxide is formed, part of which is dissolved by the alkali, and part precipitated: it may be thrown down from its alkaline solution, which is green, or black if concentrated, by dilute sulphuric acid. Heated in a retort, it is reduced, with the escape of water and oxygen gas. It slowly dissolves in the acids, most of which decompose it and resolve it into peroxide and metal: its solutions are not precipitated by sal-ammoniac. Concentrated hydrochloric acid is its best solvent. When cautiously dried, it consists of

						Berzelius.
Platinum	1	99	92·52 92·40
Oxygen	1	8	7·48 7·60
<hr/>						
Protoxide of platinum	1		107		100 00	100·00

By mixing a hot dilute solution of perchloride of platinum with a solution as neutral as possible of nitrate of suboxide of mercury, Cooper obtained a brown precipitate, which, when carefully heated, gave off calomel, and left a black powder, composed of about 95·8 platinum and 42 oxygen: he considers it as a suboxide of platinum = Pt_2O , and recommends it as the base of a good black enamel. (*Quart. Journ. of Science and Arts*, iii.) This is, however, probably a mixture of oxide of platinum and of the metal in the state of very fine division, for the proportion of oxygen varies with the mode of drying. (PHILLIPS. *Ann. Phil.*, xxii. 198.)

When sulphate of platinum is decomposed by ammonia, and the precipitate boiled in weak solution of potassa and cautiously dried, it constitutes *fulminating platinum*; when this is digested in nitric acid a grey powder remains, composed of 100 platinum, 11·36 oxygen. (E. DAVY, *Phil. Trans.*, 1820.) When spongy platinum is heated to redness in an open vessel with caustic potassa, and the product, when cold, washed with water, a grey powder is obtained, which is partly dissolved by the alkali: the residue, washed with dilute nitric acid, and afterwards with water, contains 10·5 *per cent.* of oxygen, and is regarded by E. Davy as a definite sesquioxide of platinum = Pt_2O_3 ; it is, however, generally considered as a mixture of the protoxide and peroxide.

BINOXIDE OF PLATINUM. PEROXIDE OF PLATINUM. PtO_2 . When
3 Z 2

sulphuret of platinum is digested in nitric acid, and carefully evaporated, or when perchloride of platinum is gently heated in sulphuric acid, a dark-brown solution of *persulphate of platinum* is obtained: if this solution be mixed with nitrate of baryta, sulphate of baryta is thrown down, and a nitric solution of peroxide of platinum remains; this may be in part decomposed by solution of caustic soda, which at first forms a yellow precipitate, becoming brown when carefully washed and dried, and which is a *hydrated peroxide*: if too much soda be added, a basic salt also falls. Heated in a retort, this hydrate first gives out water and becomes black; at a higher temperature it evolves oxygen, and is reduced: it has a very feeble attraction for the acids, but readily combines with many of the salifiable bases; it dissolves in the caustic and carbonated alkalis, and may be combined with lime, strontia, and baryta, by adding those earths to its acid solution, when it falls in union with them in the form of a yellow powder. (BERZELIUS.) (See also a mode of preparing this oxide, by Wittstein, *Chem. Gaz.*, Jan. 1843.) It forms a fulminating ammoniacal compound, similar to fulminating gold. This oxide consists of

						Berzelius.	Chenevix.	Richter.			
Platinum.....	1	...	99	...	86.09	...	85.87	...	87	...	89.3
Oxygen	2	...	16	...	13.91	...	14.13	...	13	...	10.7
<hr/>											
Peroxide of platinum....	1		115		100.00		100.00		100		100.0

When the alkalis are fused in contact with platinum, the metal is more or less acted on, and compounds of the alkali and oxide of platinum result. When platinum and nitre are heated together, a brown substance is formed, which, when acted on by water, is resolved into a soluble and insoluble compound of oxide of platinum and potassa. (TENNANT.)

Döbereiner has described a compound of oxide of platinum and soda = $\text{NaO}, 3\text{PtO}_2, 6\text{HO}$, which separates in the form of a red crystalline precipitate, when a solution of chloride of platinum and carbonate of soda is exposed to the sun's rays, or to a temperature of 212° . The same compound is formed by boiling the mixed solution of the two salts to dryness; it then appears as a yellow powder: when heated, it loses water and oxygen, and if the soda be dissolved out of the residue, a black powder remains, which is a mixture of platinum and its oxide. (*Ann. der Pharm.*, xiv. 21.)

When excess of lime water is added to a solution of bichloride of platinum, no precipitation ensues in the dark, but in the sun's rays the mixture becomes presently milky, and rapidly deposits a white pulverulent precipitate; in violet light the precipitate also ensues, but not in the red or yellow rays. (HERSCHEL, *Phil. Mag. and Journ.*, i. 58.) From the analysis of Weiss and Döbereiner, (*Ann. der Pharm.*, xiv. 18), it appears that this precipitate is a hydrated compound of chloride of calcium, with lime and peroxide of platinum, having the formula $\text{CaCl} + \text{CaO}, 2\text{PO}_2 + 7\text{HO}$.

PROTOCHLORIDE OF PLATINUM. PtCl . When perchloride of platinum is exposed in a porcelain capsule to a temperature not exceeding that of melting tin (about 400°), and stirred as long as it evolves chlorine, it is converted into a grey powder, insoluble in water, and not decomposed by sulphuric or nitric acids. It dissolves in boiling hydrochloric acid, and is

decomposed, as above stated, by caustic alkali, which separates protoxide. It is decomposed at a red-heat, and only gives out chlorine, without a trace of water. It consists of

						Berzelius.	Magnus.
Platinum	1	99	73·4 73·3 73·62
Chlorine	1	36	26·6 26·7 26·38
<hr/>							
Protochloride of platinum	1		135		100·0	100·0	100·00

When alcohol is added to a hot concentrated solution of this protochloride in liquid potassa, effervescence ensues from the escape of carbonic acid, and Liebig's *platinum black* is formed (p. 1060): it should be separated and washed by decantation, and dried in a porcelain capsule to avoid contact of organic matter. It becomes incandescent when moistened with alcohol, oxygen is absorbed, and acetic acid formed; and it immediately inflames a current of hydrogen in the contact of air, whence its employment already adverted to, in some of the apparatus for instantaneously lighting a spirit-lamp or taper.

PROTOCHLORIDE OF PLATINUM AND AMMONIA. When excess of ammonia is added to the hydrochloric solution of protochloride of platinum, and the mixture boiled, it becomes turbid, and deposits deep-green acicular crystals, insoluble in water and in hydrochloric acid, which contain the elements of 1 atom of protochloride of platinum and 1 of ammonia: NH_3 , PtCl . (MAGNUS.) This salt is not affected by boiling caustic fixed alkalis, nor by boiling sulphuric or hydrochloric acid; so that, as Gros observes, it is difficult to admit that it contains "ammonia in the state of ammonia." When it is digested in hot nitric acid it is converted into a white granular crystalline powder, easily soluble in water, and half the platinum of the green salt is at the same time separated in its metallic state. Neither the chlorine nor the platinum of this nitric salt can be detected by the usual tests; its elements are 1 atom of protochloride of platinum, 2 of ammonia, 1 of oxygen, and 1 of nitric acid, so that its ultimate elements are $\text{Pt}, \text{Cl}, \text{N}_3, \text{O}_6, \text{H}_6$. When a hot saturated solution of this nitric salt is mixed with sulphate of soda, the nitric acid is displaced by the sulphuric, and a corresponding sulphate obtained: and a hydrochlorate, phosphate, oxalate, &c. may be similarly formed by double decomposition. These salts are represented by Gros as containing a compound base, which he compares to ammonium, represented by $\text{Pt}, \text{Cl}, \text{N}_2\text{H}_3 = \text{B}$. The *nitrate* will then be BO, NO_5 , the *sulphate* BO, SO_3 , and the chloride BCl , &c. (*Ann. Ch. et Ph.*, LXIX. 204.)

By digesting the salt discovered by Magnus, NH_3, PtCl , in boiling ammonia, Reiset obtained a salt in yellowish crystals permanent at ordinary temperatures, becoming opaque at 230° , and not losing ammonia till heated to 482° , when a yellow compound is formed, which at a higher temperature (about 570°), is resolved into hydrochlorate of ammonia, hydrochloric acid, metallic platinum, and nitrogen. Reiset's crystals yielded on analysis $\text{N}_2\text{H}_6, \text{PtCl}$, + HO : heated to 232° they lose their atom of water, but reassume it with extraordinary rapidity from the atmosphere. At 60° the anhydrous salt is soluble in 4 parts of water, and is thrown down by alcohol and ether in the form of a white crystalline powder. Although this salt apparently includes 2 atoms of ammonia, none is evolved by the

action of the fixed alkalis at common temperature, and but little at high temperatures: its composition approaches that of the platinic combinations discovered by Gros. It gives rise to a curious set of compounds having for their base $\text{N}_2\text{H}_6, \text{PtO}, \text{HO}$, in which the HO is replaceable by an acid: thus, with a salt of silver, the chloride $\text{N}_2\text{H}_6, \text{PtCl}$, gives a precipitate of chloride of silver, and the solution, filtered and evaporated, gives crystals containing no chlorine: for instance, ($\bar{\text{A}}$ representing the acid,) $\text{N}_2\text{H}_6, \text{PtCl} + \text{AgO}, \bar{\text{A}} = \text{AgCl} + \text{N}_2\text{H}_6, \text{PtO}, \bar{\text{A}}$; and thus we obtain the *nitrate* $= \text{N}_2\text{H}_6, \text{PtO}, \text{NO}_5$; and the *sulphate*, $= \text{N}_2\text{H}_6, \text{PtO}, \text{SO}_3$. (For the details of these researches, see *Ann. Ch. et Ph.*, August, 1844.)

AMMONIO-PROTOCHLORIDE OF PLATINUM. $\text{NH}_4\text{Cl}, \text{PtCl}$, is obtained by adding 1 equivalent of sal-ammoniac to 1 of protochloride of platinum dissolved in hydrochloric acid: it forms deep-red crystals.

POTASSIO-PROTOCHLORIDE OF PLATINUM. KCl, PtCl . This salt was obtained by Magnus in the form of red anhydrous four-sided prisms, insoluble in alcohol, by evaporating a solution of protochloride of platinum and chloride of potassium in hydrochloric acid. (*Poggend.*, xiv. 241.) It consists of

Platinum	1	...	99	...	46.9	} or {	Protochloride	1	...	135	...	63.9
Potassium	1	...	40	...	19.0		of platinum					
Chlorine	2	...	72	...	34.0		Chloride of	1	...	76	...	36.1
							potassium					
	1		211		100.0			1		211		100.0

SODIO-PROTOCHLORIDE OF PLATINUM, similarly obtained, is not crystallizable, and very soluble in alcohol.

BICHLORIDE OF PLATINUM. PERCHLORIDE OF PLATINUM. PtCl_2 . When the solution of pure platinum in nitrohydrochloric acid is evaporated, it affords a deep-brown liquid which shoots into prismatic crystals consisting of hydrated perchloride of platinum and hydrochloric acid; on further evaporation it yields a brown saline mass, which becomes deeper colored upon the expulsion of its combined water. It is then a *perchloride of platinum*, yielding a deep yellow solution in water, and easily soluble in alcohol and in ether. The alcoholic solution is a useful reagent to detect the presence of potassa: the salt, the base of which is to be ascertained, is first heated to expel ammonia, in case any should be present; it is then dissolved in the smallest possible quantity of water, and mixed with the alcoholic solution of the perchloride: if it be potassa, a double salt, insoluble in alcohol, is thrown down; if not, the liquid remains clear. Of this double potassium salt, 100 parts are equivalent to 19.3 of potassa, and to 40.4 of platinum. (BERZELIUS.) Sulphurous acid and the alkaline sulphites convert this perchloride into protochloride.

Perchloride of platinum consists of

Platinum	1	...	99	...	57.8	...	Berzelius.
Chlorine	2	...	72	...	42.2	...	58.01
							41.99
Bichloride of platinum	1		171		100.0		100.00

AMMONIO-BICHLORIDE OF PLATINUM. AMMONIO-MURIATE OF PLATINUM. $\text{NH}_4\text{Cl} + \text{PtCl}_2$. This is the yellow powder which falls when solutions of bichloride of platinum and sal-ammoniac are mixed. When it is exposed to heat it loses a little water, and a compound of sal-ammoniac and protochloride of platinum is at first formed; at a red heat it evolves nitrogen, hydrochloric acid, and sal-ammoniac, without undergoing fusion, and the platinum remains in the peculiar spongy state before referred to: $3[\text{NH}_4\text{Cl}, \text{PtCl}_2] = 3\text{Pt} + \text{NH}_4\text{Cl} + 8\text{HCl} + 2\text{N}$. This ammonio-chloride is sparingly soluble in pure water; (in 150 of cold and 80 of boiling water: 1 part gives a yellow color to 20,000 of water:) it is insoluble in cold hydrochloric acid, and falls as a crystalline powder from its solution in hot hydrochloric acid. (FISCHER.) It is almost entirely insoluble in solution of sal-ammoniac, and it is insoluble in alcohol. In organic analysis it is resorted to under specific precautions as the quantitative indicator of nitrogen. If the solution from which it is precipitated contain iridium or palladium, it has a tawny-red color; these may be removed by boiling in dilute nitric acid and filtering the red solution whilst hot; as it cools it deposits a red crystalline powder, which is generally a triple salt of iridium, and from which the acid may be poured off for use as before. This double chloride, when carefully dried, contains 44 *per cent.* of platinum: it is a compound of

Platinum	1	...	99	...	44.00	} Bichloride of platinum	} 1	...	171	...	76
Chlorine	2	...	72	...	32.00						
Ammonia	1	...	17	...	7.56	} Hydrochlorate of ammonia	} 1	...	54	...	24
Hydrochloric acid ...	1	...	37	...	16.44						
<hr/>											
Ammonio-bichloride of platinum }	1		225		100.00		1		225		100

Its ultimate elements are as follows:

Platinum	1	...	99	...	44.00
Chlorine	3	...	108	...	48.00
Nitrogen	1	...	14	...	6.22
Hydrogen	4	...	4	...	1.78
<hr/>					
Ammonio-bichloride of platinum ...	1		225		100.00

POTASSIO-BICHLORIDE OF PLATINUM. $\text{KCl}, \text{PtCl}_2$. This salt is thrown down in the form of a yellow powder when concentrated solutions of chloride of potassium and of bichloride of platinum are mixed: it is very sparingly soluble in water, and is deposited from its boiling solution in small octohedral crystals: it is more soluble in heated solution of potassa, and, on cooling, does not fall till hydrochloric acid is added. (ROSE.) It readily dissolves in a warm and somewhat alkaline solution of hyposulphite of soda, and when boiled, sulphuret of platinum and sulphuric acid are formed: if the hyposulphite of soda is in excess and hydrochloric acid is added, the platinum is entirely precipitated on heating the liquor. (HIMLY, *Ann. der Pharm.*, xliii. 152). It is insoluble in alcohol. When intensely heated it evolves chlorine, and leaves a mixture of metallic platinum and chloride of potassium. Its difficult solubility renders bichloride of platinum, as already stated, a useful test of the presence of salts of potassa. It is anhydrous, and contains

Bichloride of platinum.....	1	171	69·5
Chloride of potassium	1	76	30·5
<hr/>					
Potassio-bichloride of platinum	1		247		100·0

SODIO-BICHLORIDE OF PLATINUM. $\text{NaCl}, \text{PtCl}_2$. Chloride of sodium occasions no precipitate with bichloride of platinum, but the mixed solutions yield on evaporation prismatic or tabular crystals, of a deep-orange color, soluble in water and in alcohol, and which, when heated, lose 19·25 *per cent.* of water of crystallization, and leave the anhydrous double salt: the crystals, therefore, contain

Bichloride of platinum.....	1	171	60·0
Chloride of sodium	1	60	20·8
Water	6	54	19·2
<hr/>					
Crystals of sodio-bichloride of platinum....	1		285		100·0

CALCIO-BICHLORIDE OF PLATINUM. $\text{CaCl}, \text{PtCl}_2$. Bonsdorff obtained this salt by gently evaporating a mixed solution of bichloride of platinum and chloride of calcium, the latter being in excess: it forms small prismatic crystals which lose water when heated and fall into a yellow powder: the crystals contain 8 atoms (between 24 and 25 *per cent.*) of water.

BARIO-BICHLORIDE OF PLATINUM. $\text{BaCl}, \text{PtCl}_2$. When baryta-water is gradually added to a solution of bichloride of platinum, a precipitate falls composed of baryta and peroxide of platinum (*platinate of baryta*). When the solution contains excess of baryta, it falls in the form of carbonate by exposure to air, and afterwards small crystals of the double salt are deposited. This salt is readily formed by mixing the two chlorides in atomic proportions: the crystals are orange-colored, and in form and appearance much resemble those of chromate of lead. They consist of

Bichloride of platinum.....	1	171	54·56
Chloride of barium	1	105	33·75
Water	4	36	11·69
<hr/>					
Crystals of bario-bichloride of platinum	1		312		100·00

STRONTIO-BICHLORIDE OF PLATINUM. $\text{SrCl}, \text{PtCl}_2$. This salt is obtained as the barytic salt: it forms very soluble rhombic prisms, which effloresce in the air, and include 8 atoms of water.

MAGNESIO-BICHLORIDE OF PLATINUM. $\text{MgCl}, \text{PtCl}_2$, is obtained by allowing the mixed solution of the two chlorides to evaporate spontaneously: it forms orange-colored six-sided prisms and acicular groups: they include 6 atoms of water, 4 of which they lose when heated, and crumble into a brown powder. (BONSDORFF.)

Bonsdorff has described analogous double salts of the bichloride of platinum with the chlorides of *manganese, iron, zinc, cadmium, copper, nickel, and cobalt*: their crystals are isomorphous, and consist of 1 atom of the bichloride of platinum, 1 atom of the basic chloride, and 6 atoms of water. (*Poggend.*, xvii. and xix.)

PROTIODIDE OF PLATINUM. PtI . Iodine and platinum have no direct action upon each other, but when protochloride of platinum (obtained by heating the bichloride and washing the residue with alcohol,) is digested for a quarter of an hour in a hot solution of iodide of potassium, a powder is obtained, which, when washed and dried, resembles lamp-black; it is inodorous, tasteless, and permanent till heated to about 600° , when it gives off iodine and leaves spongy platinum. It is insoluble in water and alcohol, and not acted upon by concentrated hydrochloric, nitric, or sulphuric acid. (LASSAIGNE, *Ann. Ch. et Ph.*, li. 113.) It consists of

						Lassaigne.
Platinum	1	...	99	...	44	43.95
Iodine	1	...	126	...	56	56.05
<hr/>						<hr/>
Protiodide of platinum	1		225		100	100.00

SESQUIODIDE OF PLATINUM. Pt_2I_3 . When iodide of potassium is added to a solution of oxide of platinum in hydrochloric acid, (the latter solution being in excess,) this compound falls; it should be washed in a large quantity of hot water and dried; it is a black powder which loses iodine when heated to 250° , and is entirely decomposed at a red-heat: when boiled in water it gives off a little iodine; it readily dissolves in aqueous hydriodic acid, and in solution of iodide of potassium, forming a red liquor; it is not acted on by water or alcohol, nor is it affected by cold hydrochloric, nitric, or sulphuric acid. (KANE, *Phil. Mag. and Journ.*, ii. 197.) Its components are

						Kane.
Platinum.....	2	...	198	...	34.38	35
Iodine	3	...	378	...	65.62	65
<hr/>						<hr/>
Sesquiodide of platinum....	1		576		100.00	100

BINIODIDE OF PLATINUM. PtI_2 . When the aqueous solutions of bichloride of platinum and iodide of potassium are mixed, a clear dark-red liquor is obtained, which becomes brown and turbid when heated, and on concentration deposits a black crystalline powder, which, when washed and dried, is tasteless: it is soluble (but not without some decomposition,) in alcohol, insoluble in water, and decomposed by aqueous chlorine: it combines, and forms crystallizable salts with basic metallic iodides: digested in cold aqueous hydriodic acid it yields a red liquor, which on evaporation in vacuo affords acicular crystals of a dark metallic lustre and very soluble, having the formula PtI_2, HI . (LASSAIGNE.) The components of biniodide of platinum are

						Lassaigne.
Platinum	1	...	99	...	28.21	28.09
Iodine	2	...	252	...	71.79	71.91
<hr/>						<hr/>
Biniodide of platinum	1		351		100.00	100.00

IODATE OF PLATINUM is thrown down in the form of a difficultly soluble yellow precipitate, on adding iodic acid to a solution of chloride of platinum. (PLEISCHL.)

BROMIDE OF PLATINUM. PtBr_2 . Bromine appears to have no action on platinum at any temperature, but Balard succeeded in forming

this compound by the action of a mixture of hydrobromic and nitric acid on the metal; the solution so obtained, left on evaporation a brown crystalline hydrated bibromide: it combines with the basic bromides, forming deep-red double salts.

BROMATE OF PLATINUM was obtained by Rammelsberg, (*Poggend.*, xix. 343,) by mixing solutions of sulphate of platinum and bromate of baryta, in the form of yellow solution; but on evaporation at 212° , it soon gave out oxygen gas and bromine vapor, and ultimately bibromide of platinum remained.

FLUORIDE OF PLATINUM, PtF_2 , is formed by adding fluoride of potassium to a solution of neutral bichloride of platinum, filtering, evaporating, and dissolving the residue in alcohol: it is yellow and uncrystallizable: it forms with the fluorides of ammonium, potassium, and sodium, very soluble and uncrystallizable double salts: when their solutions are evaporated, they yield gum-like residues, which, when redissolved become acid, and leave basic compounds. (BERZELIUS.)

PROTONITRATE OF PLATINUM is obtained by digesting the hydrated protoxide in dilute nitric acid: it is of a very deep brown color, and is decomposed by evaporation, leaving peroxide of platinum. (BERZELIUS.) It forms a double salt with ammonia. (REISET.)

PERNITRATE OF PLATINUM, formed by dissolving the peroxide in nitric acid, is of a dark-brown color: when evaporated to dryness, water digested upon the residue leaves a subsalt. The addition of potassa throws down half the oxide, and afterwards a double potassio-pernitrate falls. Berzelius has also described a similar soda compound.

PROTOSULPHURET OF PLATINUM. PtS . This compound may be formed, 1. By heating finely divided platinum with sulphur to redness in an exhausted glass tube. (E. DAVY.) 2. By heating ammonio-chloride of platinum with twice its weight of sulphur, to redness, in a covered crucible. (VAUQUELIN.) 3. By the mutual decomposition of protochloride of platinum and an alkaline hydrosulphuret. (BERZELIUS.) It is a grey or black powder; specific gravity 6.2 (8.2, BÖTTGER), unaltered by air or water; scarcely attacked by the boiling acids; decomposed when ignited with chlorate of potassa. It consists of

						Vauquelin.	E. Davy.	Böttger			
Platinum	1	99	85·8	84·5	84	85·51
Sulphur	1	16	14·2	15·5	16	14·49
<hr/>											
Protosulphuret of platinum	1		115		100·0		100·0		100		100·00

BISULPHURET OF PLATINUM. PtS_2 . When a solution of perchloride of platinum is mixed with sulphuret of ammonium or of potassium, a black powder falls, which, when dried in vacuo over sulphuric acid, contains, according to Berzelius, no traces of water. When this precipitate is exposed upon paper to dry in the air, the sulphur absorbs oxygen, and becomes sulphuric acid, which chars the paper. According to E. Davy, bisulphuret of platinum may be obtained by heating 3 parts of ammonio-chloride of platinum with 2 of sulphur in a small tube retort so long as gas is given off. Böttger has also given a process for the preparation of

this bisulphuret, which consists in dissolving 1 part of bichloride of platinum in 4 of absolute alcohol, in a strong wide-mouthed stopper phial, and adding 5 parts of sulphuret of carbon; the mixture, which should not occupy more than two-thirds of the phial, is well shaken and stopped, and put aside in a shady place, of medium temperature: when the mixture in about 24 hours has become dark-brown, it should be again shaken, and in about 8 days it will concrete into a black gelatinous mass of an ethereal odor: this is to be twice washed with spirit of wine (of 80 *per cent.*) to abstract sulphuret of carbon, and then rubbed down and boiled in an evaporating basin, with a large quantity of water and constantly stirred, during which an inflammable gas escapes; it is then poured upon a filter, washed with water till the washing no longer affects a solution of silver, and the residue, after having been pressed between folds of bibulous paper, is rapidly dried in vacuo over oil of vitriol, at a temperature below 260° . (*Journ. prakt. Chem.*, iii. 267.) When sulphuretted hydrogen is passed through solution of bichloride of platinum, the precipitate which falls consists of chloride and sulphuret of platinum. The color of this bisulphuret is grey, brown, or black, according to its dryness and mode of preparation: its specific gravity is about 7.2. It is only slowly attacked by nitrohydrochloric acid, even at a boiling temperature: it is soluble in aqueous solutions of alkaline hydrosulphurets, and when acted on by caustic fixed alkalis, it forms a hyposulphite of the alkali and leaves platinum. (BERZELIUS.) It consists of

					Vauquelin.	Böttger.	Berzelius.				
Platinum	1	...	99	...	75.5	...	77	...	75.11	...	75.25
Sulphur	2	...	32	...	24.5	...	23	...	24.89	...	24.75
<hr/>											
Bisulphuret of platinum	1		131		100.0		100		100.00		100.00

AMMONIO-PROTOSULPHITE OF PLATINUM. $\text{NH}_4\text{O}, \text{SO}_2 + \text{PtO}, \text{SO}_2$. When a solution of bichloride of platinum, which has been discolored by sulphurous acid gas, is neutralized by ammonia, and mixed with absolute alcohol, a white crystalline precipitate falls, constituted as above. (LIEBIG, *Chim. Org.*, i. 102. In reference to analogous combinations, see also PEYRONE, *Ann. der Pharm.*, li. 1.)

PROTOSULPHATE OF PLATINUM, PtO, SO_3 , is obtained when a solution of protoxide of platinum in caustic potassa is saturated with sulphuric acid, the liquid poured off, and the precipitate dissolved in dilute sulphuric acid: the concentrated solution is opaque and black; diluted with water it becomes red, and appears gradually to pass into persulphate. Vauquelin obtained this salt by digesting protochloride of platinum in sulphuric acid. The oxide is slowly precipitated from this sulphate by caustic alkali. (BERZELIUS.)

AMMONIO-PROTOSULPHATE OF PLATINUM. $\text{NH}_4\text{O}, \text{PtO}, \text{SO}_3$. When ammonio-iodide of platinum $[\text{NH}_3, \text{PtI}]$ is long boiled in a solution of sulphate of silver, the filtered liquor yields crystals having the above formula. Reiset and Peyrone have described another salt $= 2\text{NH}_3, \text{PtO}, \text{SO}_3$.

PERSULPHATE OF PLATINUM, $\text{PtO}_2, 2\text{SO}_3$, is obtained by acidifying the sulphur of the sulphurets of platinum by means of nitric acid. It is

of a very deep brown or almost black color, and very soluble in water, alcohol, and ether: with soda, potassa, and ammonia, it forms double salts. It is a very delicate test of the presence of gelatine, with solutions of which it forms a brown precipitate. (E. DAVY.) This salt may also be obtained by dissolving hydrated peroxide of platinum in sulphuric acid; or by adding sulphuric acid to a concentrated solution of bichloride of platinum, and evaporating to dryness. (BERZELIUS.) It remains as a black porous deliquescent mass, composed of

						Berzelius.
Peroxide of platinum	1	115	58·97 58·78
Sulphuric acid	2	80	41·03 41·22
<hr/>						<hr/>
Sulphate of peroxide of platinum	1		195		100·00	100·00

FULMINATING PLATINUM. E. Davy found that the precipitate from solution of sulphate of platinum by a slight excess of ammonia, when boiled in potassa, washed and dried, was a *fulminating platinum*; it explodes at about 420° , with a loud report, and appears to be a compound of oxide of platinum, ammonia, and water. (*Phil. Trans.*, 1817.) He has also described a compound of platinum, (*Phil. Trans.*, 1820, p. 108,) obtained by mixing equal volumes of strong aqueous solution of the sulphate and of alcohol. The color of the sulphate slowly disappears, and in some days a black substance subsides, which is washed and dried. It is also formed by boiling the sulphate and alcohol together for a few minutes. This substance is permanent in the air and insoluble in water. It detonates feebly when heated, and is not affected by chlorine, nor by nitric, sulphuric, or phosphoric acids; but it is slowly soluble in hydrochloric acid. Put into liquid ammonia, it acquires fulminating properties; and plunged into ammoniacal gas it becomes red-hot: the same phenomenon is exhibited by exposing it to the vapor of alcohol, or by placing it upon a piece of paper moistened with that fluid: in these cases the platinum is reduced with the evolution of heat, and the ignition seems to depend upon the slow combustion of the vapor of the alcohol: some of these properties correspond with those of *platinum-black* (p. 1060).

AMMONIO-PERSULPHATE OF PLATINUM. When a solution of persulphate of platinum is neutralized by ammonia and boiled, the liquor becomes colorless, and a brown powder falls, which is a basic ammonio-persulphate: it detonates feebly when heated.

POTASSIO-PERSULPHATE OF PLATINUM is a brown insoluble basic salt, formed by boiling a solution of persulphate of platinum with caustic potassa: its components are 78·32 binoxide of platinum, 10·84 sulphate of potassa, and 10·84 water. Similar basic salts with soda and with baryta have been described by E. Davy. (*Phil. Trans.*, 1820.)

PHOSPHURET OF PLATINUM. According to E. Davy, there are two phosphurets; the first, obtained by heating phosphorus with the metal in a state of fine division; they readily combine with ignition, forming a grey and somewhat crystalline substance, which does not conduct electricity: it consists of 82·5 platinum, and 17·5 phosphorus, *per cent.*, and is probably therefore Pt_2P . The second compound was formed by heating 3 parts of the ammonio-chloride of platinum with 2 of

phosphorus, to redness, in a small retort over mercury: it is a black compound with slight metallic lustre; its specific gravity is 5.28; it does not conduct electricity, and is only slightly acted on by boiling acids: it contains 70 platinum and 30 phosphorus, and appears therefore to be Pt_2P_3 . Platinum crucibles are easily injured by the phosphorus evolved during the decomposition of phosphoric salts.

SELENIURET OF PLATINUM. Selenium and finely-divided platinum combine with the evolution of heat into a grey powder, which is decomposed when heated in the air; selenium attacks platinum crucibles when evolved in them, and they may be cleansed by blowing a current of air into them when red-hot. (BERZELIUS.)

BORATE OF PLATINUM cannot be formed by double decomposition with the chlorides of platinum, inasmuch as oxide of platinum is precipitated and free boracic acid remains in the liquor. (BERZELIUS.)

CYANIDE OF PLATINUM. PtCy . When the double cyanide of platinum and mercury, PtCy, HgCy , is heated in a retort, cyanogen and mercury are evolved, and cyanide of platinum remains in the form of a green powder; it bears a moderate heat, and is insoluble in water, acids, and alkalis: heated in the air the cyanogen burns off, and platinum remains. (DÖBEREINER.)

HYDROCYANATE OF CYANIDE OF PLATINUM. PtCy, HCy . When sulphuretted hydrogen is made to act upon the double cyanide of platinum and mercury mixed with water, the cyanide of mercury is decomposed into sulphuret of mercury and hydrocyanic acid, which latter combines with the cyanide of platinum to form a compound soluble in water: the filtered solution is colorless and acid, and yields by careful evaporation green iridescent crystals. This salt sustains a temperature of 212° without decomposition, but beyond that, hydrocyanic acid is expelled and cyanide of platinum remains. The compound deliquesces in the air, and is very soluble in water and in alcohol: it is deposited from its alcoholic solution in more brilliant crystals than those obtained from the aqueous solution. When saturated with bases this hydrocyanate yields a series of double salts which have been but imperfectly examined. (REISET.)

AMMONIOCYANIDE OF PLATINUM. NH_3, PtCy . When a solution of platinamide-oxide of ammonium (Reiset's basic compound, p. 1063) is mixed with hydrocyanic acid, the above compound falls in the form of a white powder; it is difficultly soluble in boiling caustic ammonia, from which it is deposited in colorless crystals.

POTASSIOCYANIDE OF PLATINUM. $\text{KCy}, \text{PtCy}, 3\text{HO}$, is obtained, according to L. Gmelin, as follows: spongy platinum is mixed with its weight of ferrocyanide of potassium and heated to incipient redness, but not higher: the platinum separates a part of the iron from the cyanogen, and when the mass is dissolved in water the potassio-platino-cyanide may be separated by crystallization. This salt may also be obtained by evaporating the mixed solutions of chloride of platinum and ferrocyanide of potassium. Its crystals, which are long rhombic prisms, are yellow in

one direction, but blue in the direction of their axes: they effloresce and become pale-red in the air, but still retain 12·4 *per cent.* of water, which requires a higher temperature for its separation. This salt is abundantly soluble in hot water, but the greater part crystallizes as the solution cools: the solution gives a scanty white precipitate with solutions of the oxides of zinc, tin, and mercury; a pale-blue with the protosalts of iron, and a reddish-brown with the persalts of iron; a greenish blue with the salts of copper; and a white curdy precipitate which blackens by exposure to light, with nitrate of silver: it is not precipitated by nitrate of lead. This salt in crystals consists, according to Gmelin, of

Platinum	1	99	45·2
Potassium	1	40	18·4
Cyanogen	2	52	23·9
Water	3	27	12·5
<hr/>					
Potassio-cyanide of platinum.....	1		218		100·0

PLATINOPERCYANIDE OF CYANIDE OF POTASSIUM. When the preceding potassiocyanide of platinum is dissolved to saturation in hot water, and subjected whilst warm to the action of a current of chlorine, acicular crystals of a deep copper color soon begin to separate, and at length the whole concretes; as soon as this happens, the mass is drained, pressed, and dissolved in the smallest possible quantity of boiling water, to which a few drops of hydrochloric acid are previously added to decompose a little cyanate and carbonate of potassa usually present. On cooling, the salt crystallizes, and must be purified by a second and third solution in boiling water, and recrystallization. It forms small shining four-sided prisms, containing 9·94 *per cent.* of water, which, when dried upon a filter, look like filaments of copper, but are green and transparent when viewed by strong transmitted light. When heated they evolve cyanogen, become yellow, and fuse into a brown mass; they form a colorless solution with water, and are insoluble in alcohol. Sulphuric acid converts them into a yellow compound, containing platinum, potassium, and cyanogen. Alkaline carbonates decompose the cyanide of platinum, and form double cyanides. The formula of this compound is $[\text{KCy}, \text{PtCy} + \text{KCy}, \text{PtCy}_2]$ or perhaps $[2\text{KCy}, \text{Pt}_2\text{Cy}_3]$ (KNOP, *as quoted by Berzelius.*)

HYDRARGOCYANIDE OF PLATINUM. HgCy, PtCy . When the blue precipitate which falls on dropping a nitric solution of mercury into a solution of potassiocyanide of platinum is boiled in very dilute nitric acid, a white insoluble powder remains, which, according to Döbereiner, is the above double cyanide of mercury and platinum: it dissolves in boiling hydrochloric acid, without evolving hydrocyanic acid; the caustic alkalis dissolve the cyanide of platinum, and decompose the cyanide of mercury, leaving oxide of mercury. This salt combines with the nitrates of both oxides of mercury to form a species of triple salts. (BERZELIUS.)

SULPHOCYANIDE OF PLATINUM forms, according to Grotthuss, a bulky flocculent precipitate of a yellow color: it is soluble in acids and in solutions of chloride of potassium and sodium, and of sal-ammoniac: alcohol throws it down again from these solutions.

ALLOYS OF PLATINUM. With *potassium* and *sodium* it forms compounds which decompose water. (DAVY.) Its alloy with *manganese* is unknown. *Iron* and platinum in equal parts form a crystalline alloy which takes a fine polish. According to Dr. Lewis, the alloy of cast iron and platinum is hard, tough, and somewhat ductile, the density greatly exceeding the mean: it is brittle when hot. Stodart and Faraday found the toughness and smoothness of steel improved by one-hundredth of platinum. (*Phil. Trans.*, 1822.) When wires of steel and platinum are welded together and polished, they exhibit a damasked surface, especially when the steel parts are slightly acted upon by dilute acid. This welding property of platinum may be usefully applied in the arts; wires may be joined so as to form rings and chains; and, with a view to economy, platinum may be joined to iron or steel for many uses in the laboratory of the chemist. Iron combined with 1 *per cent.* of platinum, is not attacked by common nitric acid. (SCHÖNBEIN. See also BOUSSINGAULT, *Ann. Ch. et Ph.*, liii. 441.) Platinum dissolves in fused *zinc*; the alloy is bluish-white, brittle, and hard: one-twentieth of platinum destroys the malleability of zinc, and one-fourth of zinc renders platinum brittle. (LEWIS.) A morsel of zinc heated in platinum-foil before the blow-pipe burns vividly and even with explosion. *Tin* and platinum combine in all proportions, forming alloys more or less brittle and fusible. When tin-foil and platinum are wrapped together and heated by the blow-pipe, they combine with incandescence. (Fox, *Ann. Phil.*, xiii. 467. *On the separation of platinum and gold from tin and arsenic*, see ELSNER, *Journ. für prakt. Chem.*, xxxv. 314: *Chem. Gaz.*, Jan. 1846.) The alloy of *cadmium* and platinum is white, granular, brittle, and easily fusible: heated till the excess of cadmium is expelled, it contains 100 platinum + 117 cadmium, = Pt, Cd_2 . (STROMEYER.) The alloy of *cobalt* and platinum is comparatively fusible. With its weight of *nickel* platinum forms a pale yellow alloy, susceptible of a high polish, and obedient to the magnet. *Copper* and platinum form alloys, the ductility and color of which, vary with the proportions: platinum easily destroys the color of copper: this compound has been recommended for the mirrors of reflecting telescopes: an alloy of 7 platinum, 16 copper, 1 zinc, resembles gold in color. (COOPER, *Quart. Journ.*, iii. 119.) *Lead* and platinum form brittle alloys, not entirely decomposed by cupellation. Platinum and lead-foil folded together and heated before the blow-pipe combine with elevation of temperature. (DUMAS.) *Antimony* forms a grey compound with platinum, partly decomposed by heat; and entirely, by roasting: these metals enter into ignition when they combine, in the same manner as tin and zinc. (Fox.) *Bismuth* and platinum form brittle alloys not entirely decomposed by cupellation. (LEWIS.) *Arsenic* and platinum form a dark-grey, brittle alloy. When particles of arsenic are placed upon red-hot platinum-leaf, they immediately fuse a hole in it. When 2 parts of platinum, 2 of arsenious acid, and 1 of potassa, are fused together, a compound of 89 platinum, and 10 of arsenic, is obtained: its density is 16.4; it is fusible at a red-heat, but the whole of its arsenic cannot be expelled by heat; 100 parts of spongy platinum heated with excess of arsenic yield 174 of alloy. (GMELIN.) Equal parts of *molybdenum* and platinum melted into a hard, brittle mass: when the proportion of platinum was increased, the fusion was not complete. (HIELM.) *Mercury*

amalgamates difficultly with platinum: a compound of 63 of mercury, and 37 of platinum, is a soft solid: spongy platinum forms the readiest combination, especially when rubbed with the mercury in a hot mortar; or moistened with dilute acetic acid. When the amalgam of sodium is put into a concentrated solution of chloride of platinum, or triturated with ammonio-chloride of platinum and water, a platinum amalgam is also formed: this amalgam adheres well to the surface of glass, and may be used for plating copper, silver, or gold. *Silver* and platinum form fusible and ductile alloys; when the silver predominates they are soluble in nitric acid; by boiling sulphuric acid, the silver only is dissolved. When the alloy is kept in fusion, its components have a tendency to separate. *Gold* and platinum require a strong heat for combination, and the color of the gold is greatly deteriorated even by one-twenty-second part of platinum: an alloy of 4 of platinum, and 1 of gold, nearly resembles platinum in color; the gold color does not predominate till it forms eight-ninths of the alloy. (HATCHETT. KLAPROTH.)

The perfection with which vessels of platinum resist the action of heat and air, of most of the acids, and of sulphur and mercury, renders them peculiarly valuable in many of their applications; but its high value is against its very general adoption, for, although much cheaper than gold, it is worth between four and five times its weight of silver. Berzelius observes (*Lehrbuch*), that in the employment of platinum vessels, the following precautions must be attended to: 1. They must not be subjected to the action of compounds which evolve chlorine. 2. Nitre, and the alkalis, must not be fused in them. 3. No metallic reductions must be performed in them; nor compounds of phosphorus decomposed so as to evolve that substance. 4. When metallic oxides are heated in a platinum crucible, the heat must not be raised beyond redness, provided the oxide is easily decomposed: hence the caution requisite with the oxides of lead, bismuth, copper, cobalt, nickel, and antimony, which, though they may not effect the fusion of the crucible, spoil it by their action upon its interior surface, which is rendered rough and porous. 5. That the immediate contact of the fuel (charcoal should always be used) with the crucible should be avoided as much as possible, especially at very high temperatures; for it is thus, in the process of time, rendered brittle and unsound. Small holes and fissures may be filled up and soldered with pure gold, but in that case the vessel must not be exposed to a white-heat, because then the gold and platinum combine. It would appear from Daniell's experiments (*On a new register pyrometer*, *Phil. Trans.*, 1831, p. 315), that one cause of the brittleness which platinum acquires when repeatedly heated in the usual fuel, depends upon the absorption of silicium, to the amount of about 3 *per cent.* A high temperature appears necessary to effect this combination, which is somewhat analogous to the absorption of carbon by iron in the process of making steel by cementation.

CHARACTERS OF THE SALTS OF PLATINUM. The color and the difficult solubility of the ammonio and potassio-chlorides of platinum, and the solubility of the corresponding soda-compounds, are very characteristic of this metal. Phosphate of soda produces no precipitate in chloride of platinum; the ferrocyanides of potassium throw down the platino-chloride of potassium: cyanide of mercury occasions no precipitate: iodide of potas-

sium communicates a reddish-brown color to solutions of the chlorides of platinum, and gradually produces a brown precipitate; and if the mixture be heated in a matrass, the glass acquires a coating of metallic platinum. All the metals which reduce the chloride of gold, with the exception of palladium, act similarly upon chloride of platinum, but its complete separation in the metallic state is slow: iron, zinc, cadmium, and copper, are its most effective precipitants; they separate it as a black powder, which sometimes adheres in films to the glass.

§ XXXIV. PALLADIUM. Pd. 54.

PALLADIUM was discovered by Wollaston in 1803: it is associated with the other metals mentioned in the last section as constituting the ore of platinum: it has also been found by M. Zinken in the gold and lead ores of the duchy of Anhalt Bernburg (*Ann. Ch. et Ph.*, XLiv. 201), and is common in Brazilian gold. Small fibrous grains of *native palladium* were found by Wollaston in some of the South American platinums.

Palladium is separated from the ore of platinum by the following process. (WOLLASTON, *Phil. Trans.*, 1805.) Digest the *ore* in nitrohydrochloric acid, neutralize the redundant acid by soda, throw down the platinum by sal-ammoniac, and filter: to the filtered liquor add a solution of cyanide of mercury: a yellow flocculent precipitate of *cyanide of palladium* is soon deposited, which yields palladium on exposure to heat.

The extraction of palladium from the auriferous sand of Brazil consists in fusing it with silver, by which a quaternary alloy of gold, palladium, silver, and copper is obtained, which is granulated by pouring it into water, and digested in nitric acid, by which the gold is separated from the soluble metals: from the solution the silver is precipitated by common salt, and the copper and palladium by plates of zinc: the deposit of these metals is redissolved in nitric acid, and the solution precipitated by excess of ammonia, which redissolves the oxides of copper and palladium: when this ammoniacal solution is saturated by hydrochloric acid, a double ammonio-chloride of palladium is deposited in the form of a yellow crystalline powder, which when calcined leaves spongy palladium. (*Phil. Mag.*, November, 1843.)

To obtain malleable palladium, Dr. Wollaston gives the following more explicit directions. (*Phil. Trans.*, 1819.) "The residuum obtained from burning the cyanide of palladium is to be combined with sulphur, and each cake of the sulphuret, after being fused, is to be finally purified by cupellation, in an open crucible, with borax and a little nitre. The sulphuret is then to be roasted, at a low red-heat, on a flat brick, and pressed, when reduced to a pasty consistence, into a square or oblong and perfectly-flat cake. It is again to be roasted very patiently, at a low red-heat, until it becomes spongy on the surface. During this process sulphur flies off in the state of sulphurous acid, especially at those moments when the heat is allowed occasionally to subside. The ingot is then to be cooled; and when quite cold, is to be tapped with a light hammer, in order to condense and beat down the spongy excrescences on its surface.

The alternate roastings and tappings (or gentle hammerings) require the utmost patience and perseverance, before the cake can be brought to bear hard blows; but it may, by these means, at length be made so flat and square, as to bear being passed through the flattening-mill, and so laminated to any required degree of thinness. Thus prepared, it is always brittle while hot, possibly from its still containing a small remnant of sulphur. I have also fused some palladium *per se*, without using sulphur; but I have always found it, when treated in this way, so hard and difficult to manage, that I greatly prefer the former process."

Palladium is of a dull-white color, malleable and ductile. Its specific gravity is about 11.3, or 11.86 when laminated. Its specific heat is 0.05927. (REGNAULT.) It is hard. It fuses at a temperature above that required for the fusion of gold, and when intensely heated by the oxy-hydrogen blow-pipe, it is dissipated in sparks. When heated over the flame of a spirit-lamp, it acquires various shades of blue upon its surface, in consequence of superficial oxidation. It is acted on by the greater number of the acids when aided by heat, and also by potassa and nitre: it is blackened when an alcoholic solution of iodine is evaporated from its surface, which is not the case with platinum: it has a strong affinity for cyanogen. The equivalent of palladium appears to be somewhere between 52 and 57. I have adopted 54. (53.3 TURNER. GMELIN.)

PROTOXIDE OF PALLADIUM. PdO . By carefully heating the protonitrate of palladium to dull redness, a black oxide is obtained, which dissolves in hydrochloric acid without evolving chlorine. When nitrate of palladium is precipitated by an alkali, the red or dark-orange colored powder which falls, is an *hydrated oxide*. In this state it is readily soluble in the acids, yielding red and brown salts of a purely astringent taste. This oxide consists of

						Berzelius.
Palladium	1	54	87.09 86.94
Oxygen	1	8	13.91 13.06
<hr/>						<hr/>
Protoxide of palladium....	1		62		100.00	100.00

BINOXIDE OF PALLADIUM. PdO_2 . To prepare this oxide a solution of potassa, or its carbonate, in excess, should be poured by little and little on the solid bichloride of palladium and potassium, and the materials well intermixed; water is not first added, because it decomposes the double chloride, and the alkali is not added all at once, because the oxide would then be dissolved at first, and afterwards separate as a gelatinous hydrate, which could not be purified by washing. When prepared according to the foregoing directions, the binoxide is obtained as a hydrate, of a deep yellowish-brown color, which retains a little potassa in combination: when boiled in water it becomes black and nearly anhydrous. In its anhydrous state this oxide is quietly reduced at a red-heat, but the reduction of the hydrate ensues at the same temperature with explosive violence. (BERZELIUS.) Its components are

						Berzelius.
Palladium	1	54	77.14 76.90
Oxygen	2	16	22.86 23.10
<hr/>						<hr/>
Bin oxide of palladium	1		70		100.00	100.00

PROTOCHLORIDE OF PALLADIUM, PdCl , is obtained (1.) by digesting palladium in hydrochloric acid with a little nitric acid, and evaporating to dryness: it forms a brown powder, which is nearly black when rendered anhydrous. (BERZELIUS.) 2. By heating sulphuret of palladium in a stream of gaseous chlorine, when it is obtained in the form of a red crystalline compound, part of which forms a rose-colored sublimate. (FELLENBERG.) When highly heated it evolves chlorine, and is readily decomposed when heated in a stream of hydrogen, forming hydrochloric acid, and leaving palladium: it forms double salts with the basic metallic chlorides, which are soluble in water and in alcohol. When this chloride is decomposed by a small quantity of alkali, a hydrated basic oxichloride in the form of an insoluble brown powder is produced $= \text{PdCl} + 3\text{PdO} + 4\text{HO}$. Heated to about 600° , it abandons half its chlorine, and *subchloride of palladium* remains as an olive-brown insoluble powder. (KANE.) When tartaric acid is added to a solution of chloride of palladium, the liquor is not precipitated by excess of soda; but if a little alcohol be added and the mixture boiled, metallic palladium falls. The components of protochloride of palladium are

						Fellenberg.
Palladium	1	...	54	...	60	60.2
Chlorine	1	...	36	...	40	39.8
<hr/>						<hr/>
Protochloride of palladium....	1		90		100	100.0

AMMONIO-PROTOCHLORIDES OF PALLADIUM. These compounds have been described by Fehling (*Ann. der Pharm.*, xxxix.), and by Kane. When a solution of protochloride of palladium is mixed with caustic ammonia, a flesh-colored precipitate falls, which is NH_3, PdCl . It may be heated to 350° without change after it has been carefully dried, but when moist, it acquires a yellow color at 212° . This yellow modification may be obtained in small crystals by heating the original flesh-colored precipitate in its mother-liquor, when it dissolves and crystallizes on cooling. When either of these modifications is dissolved in ammonia, and evaporated, colorless prisms are deposited $= 2\text{NH}_3, \text{PdCl}, \text{HO}$; these when gently heated lose water and 1 atom of ammonia, and leave the yellow modification. Kane has also described other basic ammonio-chlorides.

When a solution of protoxide of palladium in hydrochloric acid is mixed with sal-ammoniac and evaporated, iridescent prismatic crystals are obtained, which give a red solution with water, and are insoluble in alcohol: they are $\text{NH}_4 \text{Cl}, \text{PdCl}$. (WOLLASTON.)

PALLADIO-PROTOCHLORIDE OF POTASSIUM. KCl, PdCl . This salt is formed when palladium is boiled in hydrochloric acid with the addition of nitre, or when the component chlorides are dissolved in water in atomic proportions, and the solution evaporated: it forms greenish-brown prisms, which give a red solution in water, and are insoluble in alcohol: when boiled with dilute alcohol, the metal is reduced. This salt contains about 32.5 palladium *per cent.* The *palladio-protochloride of sodium* is deliquescent, and very soluble in water and alcohol. Bonsdorff has described a number of other palladio-protochlorides.

BICHLORIDE OF PALLADIUM. PERCHLORIDE OF PALLADIUM. PdCl_2 , is only known in solution; it is formed by dissolving the protochloride in nitrohydrochloric acid, and applying a gentle heat: the solution is almost black, and gives a characteristic red precipitate with chloride of potassium; when the solution is either diluted, or boiled, chlorine is evolved, and protochloride formed. The components of bichloride of palladium are

Palladium.....	1	54	42.8
Chlorine	2	72	57.2
<hr/>					
Bichloride of palladium	1		126		100.0

PALLADIO-BICHLORIDE OF POTASSIUM. $\text{KCl}, \text{PdCl}_2$. When the palladio-protochloride of potassium is digested in nitrohydrochloric acid and evaporated to dryness, the above compound is obtained in the form of a red crystalline powder: it is very sparingly soluble in cold water, and hot water partially decomposes it with the formation of hydrochloric acid and binoxide of palladium: heated till it fuses, it evolves chlorine, and becomes the protosalt. The palladio-bichloride of ammonium ($\text{NH}_4 \text{Cl}, \text{PdCl}_2$) is also of a cinnabar-red color.

IODIDE OF PALLADIUM, PdI , is thrown down by iodide of potassium from a solution of protochloride of palladium; when dried in vacuo it is a black tasteless substance: at about 570° it begins to lose iodine; it is insoluble in water, alcohol, ether, and aqueous hydriodic acid: it consists of

						Lassaigne.
Palladium.....	1	54	30 29.72
Iodine	1	126	70 70.28
<hr/>						<hr/>
Iodide of palladium	1		180		100	100.00

Iodide of palladium forms a nearly colorless or pale yellow solution in aqueous ammonia, which on exposure to air deposits yellow crystals $= \text{NH}_3, \text{PdI}$: the same compound falls as an orange-colored powder when the excess of ammonia is saturated by an acid. When in this state it is boiled in water, it passes into a red crystalline powder: boiled in nitric acid it is resolved with the evolution of iodine into protonitrate of palladium. In a hot and strong solution of ammonia, or exposed to an atmosphere of gaseous ammonia, it forms a colorless compound $= 2\text{NH}_3, \text{PdI}$. (FEHLING. *Ann. der Pharm.*, xxxix.)

IODATE OF PALLADIUM. Iodate of potassa forms an abundant yellow precipitate when added to a solution of protochloride of palladium. (PLEISCHL.)

BROMIDE OF PALLADIUM. A solution of palladium in nitrohydrobromic acid leaves a brown residue on evaporation, insoluble in water but soluble in hydrobromic acid. It forms dark-brown salts with the basic bromides. The hydrated protoxide of palladium is sparingly soluble in bromic acid. (RAMMELSBERG. *Poggend.*, xix. and lv.)

FLUORIDE OF PALLADIUM is a brown compound, formed by the action of hydrofluoric acid on neutral protonitrate of palladium. (BERZELIUS. *Lehrbuch*, iii. 964.)

NITRATE OF PALLADIUM. Palladium, when aided by heat, dissolves slowly in nitric acid, forming a brown solution which leaves a brown subnitrate on evaporation. Nitrate of protoxide of palladium forms a double salt with ammonia.

SULPHURET OF PALLADIUM. PdS. This compound is readily formed by fusing sulphur with palladium; it is white, hard, and fusible, and when long exposed to heat and air, loses the whole of its sulphur. It is thrown down in the form of a black powder, by the action of sulphuretted hydrogen upon the salts of palladium. Heated in a stream of chlorine, it yields chloride of sulphur and protochloride of palladium. It consists of

						Fellenberg.	Berzelius.	Vauquelin.
Palladium	1	54	77.1	75.65 78
Sulphur	1	16	22.9	24.35 22
<hr/>								
Sulphuret of palladium	1		70		100.0		100.00	100
								100.0

PROTOSULPHATE OF PALLADIUM, PdO,SO₃, is obtained by boiling the protonitrate to dryness with sulphuric acid; also by boiling the metal in sulphuric acid, when sulphurous acid is evolved, and a brown solution is obtained, which deposits the sulphate in red crystals. This salt dissolved in aqueous ammonia yields two *ammonio-sulphates* = NH₃,PdO,SO₃ and 2NH₃,PdO,SO₃. (KANE.)]

PHOSPHURET OF PALLADIUM is a fusible compound.

PHOSPHATE OF PALLADIUM falls in the form of a pale-yellow precipitate, on mixing solutions of protonitrate of palladium and phosphate of soda.

SELENIURET OF PALLADIUM. Selenium and palladium combine, with the evolution of heat; the compound is grey and coherent, but does not easily fuse: before the blow-pipe it gives off selenium, and at a very high temperature melts into a grey metallic button, which is brittle and crystalline, and still retains selenium.

CARBURET OF PALLADIUM. Palladium acquires extreme brittleness when long fused in contact with charcoal. When a plate of palladium is long held in the flame of alcohol, it becomes covered with carbon, and carbonaceous excrescences gradually form upon it, which, when burned, leave palladium, and the surface of the metal becomes corroded, and its whole substance brittle. When spongy palladium, in the state in which it is obtained by the ignition of its ammonio-chloride, is heated to redness, and placed upon the wick of a spirit-lamp, it glows and becomes enveloped in an accumulation of a compound of carbon and palladium. This property of precipitating charcoal from flame, and combining with it, is peculiar to palladium; platinum and iron only show slight indications of it. (WÖHLER, *Poggend.*, iii. 71.)

CARBONATE OF PALLADIUM. Berzelius has described a highly basic carbonate $= 10\text{PdO}, \text{CO}_2, 10\text{HO}$: if this compound exist, it is probably $\text{PdO}, \text{CO}_2, \text{HO} + 9\text{PdO}, \text{HO}$.

CYANIDE OF PALLADIUM. PdCy . This compound is formed when a solution of cyanide of mercury is added to a neutral solution of palladium: it falls in olive-colored or dingy-yellow flakes: this furnishes a ready method of separating palladium from other metals which are incapable of decomposing the cyanide of mercury. The cyanide of palladium, when sufficiently heated, leaves the metal: it dissolves in cyanide of potassium, and, on evaporation, prismatic crystals of *palladio-cyanide of potassium* are obtained. There is also a corresponding *ammoniacal salt*. When nitrate of palladium is decomposed by cyanide of mercury, the precipitate deflagrates by heat.

SULPHOCYANIDE OF PALLADIUM is a very soluble salt.

ALLOYS OF PALLADIUM. These have not been minutely examined. It combines very energetically with arsenic, and with antimony, and forms alloys which are easily fusible and brittle. Analogous alloys may be formed with zinc, tin, and lead, all of which produce ignition on combination. Equal parts of palladium and bismuth form a brittle but very hard alloy, of the sp. gr. 12.5. The alloy with iron is brittle, and in the proportion of 1 *per cent.* it improves the quality of steel for certain cutting instruments. (FARADAY and STODART.) The alloy of 1 part of palladium with 4 of copper is white and ductile: equal parts of the two metals give a hard brittle compound, sp. gr. 10.39. By agitating a solution of a palladium salt with excess of mercury, a soft amalgam is produced, but if the palladium is in excess, it is a grey powder containing 2 atoms of palladium to 1 of mercury: it requires a white heat to expel the mercury. Like platinum, it destroys the color of gold; 1 part, fused with 6 of gold, forming a white alloy. This compound, from its hardness and durability, was employed, at the suggestion of Dr. Wollaston, for the graduated part of the mural circle, constructed by Troughton for the Royal Observatory at Greenwich. Electroplating with palladium is easily performed, and in some cases usefully applicable.

CHARACTERS OF THE SALTS OF PALLADIUM. The fixed alkalis throw down red or orange-colored precipitates from the solutions of palladium, sparingly soluble in excess of the alkali. Ferrocyanide of potassium gives an olive-green precipitate; and sulphuretted hydrogen one of a dark-brown color. Protochloride of tin occasions a brown precipitate in the neutralized solutions of palladium; when dilute, the mixture becomes green. Protosulphate of iron throws down metallic palladium. Many of the other metals precipitate palladium in the metallic state. Cyanide of mercury forms a precipitate in all the salts of palladium when the acid is not in excess. Iodide of potassium occasions a black precipitate of iodide of palladium in very dilute solutions. Chloride of palladium added to a solution of 1 part of iodide of potassium in 400,000 of water produces a brown tint. (LASSAIGNE.)

§ XXXV. RHODIUM. R. 52.

THIS metal, discovered in 1803, by Wollaston, may be obtained as follows: Digest the *ore* of platinum in nitrohydrochloric acid, filter the saturated solution, and pour it into a solution of sal-ammoniac, by which the greater proportion of the platinum is precipitated; filter, and separate the palladium by cyanide of mercury; filter again, and immerse a plate of zinc into the clear solution, which will become coated with a black powder. Separate this and digest it in dilute nitric acid, by which a little copper and lead are taken up. Then wash, and digest in dilute nitrohydrochloric acid, to which add some common salt; evaporate to dryness, and wash the dry mass repeatedly with alcohol. A deep-red substance remains, which is a rhodiochloride of sodium, and which, when dissolved in water, furnishes a black precipitate upon the immersion of a plate of zinc; this, strongly heated with borax, assumes a white metallic lustre, and is rhodium: or the double chloride may be heated white-hot, and boiled in water, when finely-divided metallic rhodium remains. According to Berzelius it is most effectually reduced when heated in a stream of hydrogen gas.

Rhodium is a white metal very difficult of fusion; its specific gravity is about 11; it is extremely hard: it does not admit of welding, so that it can only be obtained in adherent masses by exposing its fused sulphuret or arsenuret to a white-heat till the arsenic and sulphur are expelled; it then remains as a vesicular silver-colored mass. When pure, the acids do not dissolve it, but they act upon and dissolve several of its alloys, a circumstance which explains its presence in the nitrohydrochloric solution of platinum. When an alloy of lead and rhodium is digested in nitrohydrochloric acid, it is also readily dissolved, and by evaporation a red compound is obtained, from which chloride of rhodium may be separated by water. The *red color* of this compound suggested the name which has been applied to the metal (from $\rho\acute{o}\delta\delta\omicron\nu$, a rose). Berzelius has shown that metallic rhodium may be oxidized by ignition either with nitre or with bisulphate of potassa, and that when heated with the latter, a double sulphate of peroxide of rhodium and potassa is produced, which yields a yellow solution with hot water: in this way rhodium may be separated from platinum, iridium, and osmium. There is some discrepancy in the equivalent of rhodium given by different chemists; according to the latest experiments of Berzelius, the number 52 has been adopted. (52 GMELIN. 52.2 TURNER. 54 THOMSON.)

RHODIUM AND OXYGEN. Rhodium may be oxidized by the joint action of heat and air, but the protoxide, $= RO$, has not been obtained and examined in an isolated state. The salifiable oxide is $R_2 O_3$.

SESQUIOXIDE OF RHODIUM. PEROXIDE OF RHODIUM. RHODIC OXIDE. $R_2 O_3$. This oxide is obtained, (1.) By heating finely-divided rhodium with caustic potassa and a little nitre to redness in a silver crucible, washing the product and digesting it in hydrochloric acid: a greenish-grey hydrated oxide remains, which, however, is insoluble in acids. (2.) An excess of carbonate of potassa, or carbonate of soda, is added to a solution

of rhodiochloride of potassium or sodium, and the mixture evaporated: it immediately becomes turbid, and during evaporation, gelatinous, from the formation of hydrated oxide, which is to be thrown upon a filter and well washed: in this state it retains alkali, and is soluble in the acids, which acquire a yellow color, and form double salts: when the hydrochloric solution, which also is at first yellow, is evaporated, it reddens when concentrated, and leaves a red residue.

This oxide of rhodium, when rendered anhydrous by long exposure to a red-heat, (when, according to Berzelius, it loses no oxygen,) is black: it is very easily reduced by hydrogen. Its components are

						Berzelius.
Rhodium	2	104	81.25 81.28
Oxygen	3	24	18.75 18.72
<hr/>						
Sesquioxide of rhodium	1		128		100.00	100.00

PROTOCHLORIDE OF RHODIUM. RCl , was obtained by Fellenberg by passing dry chlorine over heated protosulphuret of rhodium: it is a red compound, easily reduced when gently heated in a stream of hydrogen, but not altered by the continued action of chlorine: it is insoluble in water and in hydrochloric and nitric acids, and is not decomposed by a boiling solution of potassa or carbonate of potassa. (FELLENBERG.) It consists of

						Fellenberg.	Berzelius.
Rhodium....	1	52	59.09 59.49 60
Chlorine	1	36	40.91 40.51 40
<hr/>							
Protochloride of rhodium.	1		88		100.00	100.00	100

SESQUICHLORIDE OF RHODIUM. R_2Cl_3 . Berzelius obtained this salt by adding fluosilicic acid (not in excess) to an aqueous solution of rhodiochloride of potassium, filtering, evaporating, dissolving the residue in water, and evaporating again, with the addition of hydrochloric acid, to expel adhering fluosilicic acid. This is a dark-brown uncrySTALLINE compound, which is decomposed at a high red-heat into chlorine and metal: it gradually deliquesces on exposure to air, and forms a red solution with water, and with alcohol. It forms a yellow solution with hydrochloric acid, which reddens as the excess of acid is expelled by evaporation. Berzelius has described another chloride = R_4Cl_5 , obtained by passing chlorine over finely-divided rhodium, as obtained by reducing an alkaline rhodiochloride by hydrogen: it is a red powder, insoluble in water and hydrochloric acid: it is probably either the protochloride, or a compound of it with the perchloride = $2RCl + R_2Cl_3$. Sesquichloride of rhodium consists of

Rhodium	2	104	49.05
Chlorine	3	108	50.95
<hr/>					
Sesquichloride of rhodium	1		212		100.00

RHODIOCHLORIDE OF AMMONIUM. AMMONIO-SESQUICHLORIDE OF RHODIUM. $2NH_4Cl, R_2Cl_3$. This double salt is obtained by evaporating a mixed solution of chloride of rhodium and sal-ammoniac: it forms brilliant garnet-colored prisms, which, when decomposed by heat, leave 31 *per cent.* of rhodium (VAUQUELIN. *Ann. de Chim.*, xc. 204): they give a red

solution in water, and are insoluble in alcohol. Bichloride of platinum, added to their aqueous solution, throws down ammonio-bichloride of platinum, and chloride of rhodium (hydrochlorate of oxide of rhodium) remains in solution. The crystals of this salt consist of

Chloride of ammonium	2	...	108	...	31.92
Sesquichloride of rhodium.....	1	...	212	...	62.72
Water	2	...	18	...	5.36
<hr/>					
Rhodiochloride of ammonium	1		338		100.00

RHODIOCHLORIDE OF POTASSIUM. $2\text{KCl}, \text{R}_2\text{Cl}_3$. This salt is best obtained by passing a stream of chlorine over a mixture of equal parts of finely divided rhodium and chloride of potassium, heated to dull redness in a glass tube, till chlorine ceases to be absorbed: the product is dissolved in water, and alcohol added to the filtered solution: the red precipitate of rhodiochloride is further washed with dilute alcohol, (sp. gr. 840), to free it from remaining chloride of potassium. This salt may be obtained by evaporation in the form of black-red quadrilateral prisms, which are $= 2\text{KCl}, \text{R}_2\text{Cl}_3, 2\text{HO}$: they lose their water of crystallization at a little above 212° . The anhydrous salt contains about 29 *per cent.* of rhodium, its proximate components being

						Berzelius.	
Chloride of potassium.....	2	...	152	...	41.76	...	41.54
Sesquichloride of rhodium ...	1	...	212	...	58.24	...	58.46
<hr/>							
Rhodiocliloride of potassium	1		364		100.00		100.00

RHODIOCHLORIDE OF SODIUM. $3\text{NaCl}, \text{R}_2\text{Cl}_3$. This salt is obtained as the preceding, but 2 parts of chloride of sodium and 1 of pulverulent rhodium are used. The crystals obtained from its aqueous solution include 18 atoms (30 *per cent.*) of water; they are red, fusible in their water of crystallization, and effloresce in a dry atmosphere. After a long exposure to a red-heat, they leave a mixture of metallic rhodium and chloride of sodium. They dissolve in 1.5 parts of water, forming a cochineal-red solution; they are insoluble in alcohol: their components are

Chloride of sodium'.....	3	...	180	...	32.71	3	...	180	...	45.92
Sesquichloride of rhodium	1	...	212	...	38.54	1	...	212	...	54.08
Water	18	...	162	...	28.75							
<hr/>												
Crystallized.....	1		554		100.00	Anhydrous	1		392		100.00	

NITRATE OF RHODIUM is formed by dissolving the oxide in nitric acid; it is deliquescent, uncrystallizable, and of a deep red color. The metal is thrown down from it by copper and mercury, but not by silver. (WOLLASTON.) The double *nitrate of rhodium and soda* forms dark-red crystals, soluble in water, but insoluble in alcohol. (BERZELIUS.)

PROTOSULPHURET OF RHODIUM, RS , is obtained by heating the metal in a state of fine division with sulphur; or by heating the ammonio-chloride of rhodium with sulphur; it is also formed by heating the solution of the latter salt with one of an alkaline hydrosulphuret, washing the precipitate with boiling water, and subjecting it at a red-heat to a cur-

rent of carbonic acid gas, by which water and a portion of sulphur are carried off. (FELLENBERG. *Poggend.*, L. 63.) This sulphuret is a bluish metallic compound, which, when heated in the air, gives off sulphurous acid and leaves spongy rhodium: heated in a stream of chlorine, it yields chloride of sulphur and protochloride of rhodium: it consists of

						Fellenberg.	Vauquelin.
Rhodium	1	...	52	...	76.47	76.52	79.36
Sulphur.....	1	...	16	...	23.53	23.48	20.64
<hr/>							
Protosulphuret of rhodium	1		68		100.00	100.00	100.00

SESQUISULPHURET OF RHODIUM. R_2S_3 . Hydrosulphuret of ammonia produces a brown precipitate in solution of rhodochloride of sodium, which becomes acid when exposed to air, and is perfectly soluble in solution of sulphuret of potassium: it is only partially soluble in solution of caustic potassa, with the formation of hyposulphurous acid and deposition of rhodium. (BERZELIUS.)

SULPHATE OF SESQUIOXIDE OF RHODIUM is a brown soluble uncrystallizable salt, obtained by the action of nitric acid on the precipitated sesquisulphuret of rhodium: by careful heating, sulphuric acid and oxygen may be so expelled as to leave a protosulphate. Sesquioxide of rhodium forms two double sulphates with potassa; one is obtained by igniting rhodium with bisulphate of potassa; it yields a yellow solution with hot water; the other is formed by the action of sulphurous acid on the rhodochloride of potassium; it is a pale yellow powder. (BERZELIUS.)

PHOSPHATE OF SESQUIOXIDE OF RHODIUM is formed by boiling pulverulent rhodium in concentrated phosphoric acid, or by fusing it at a red-heat with the hydrated acid. The product yields a yellow-brown solution. (FISCHER. *Poggend.*, xxiii. 257.)

ALLOYS OF RHODIUM. Rhodium forms malleable *alloys* with the malleable metals, several of which have been examined by Dr. Wollaston. (*Phil. Trans.*, 1804.) 1 to 2 *per cent.* of rhodium gives *steel* great hardness, and yet there is sufficient tenacity to prevent cracking either in forging or hammering. (*Quart. Journ.*, ix. 328.) The alloy of 1 part of rhodium and 2 of *lead* has the sp. gr. 11.3: with 3 of lead the alloy is perfectly soluble in nitric acid: so also is the alloy of 1 of rhodium and 3 of *copper*, and 1 of rhodium and 3 of *bismuth*. When its alloy with *arsenic* is heated to redness exposed to air, the arsenic evaporates and leaves brittle rhodium. With *silver* it forms a malleable alloy, which, on slow cooling, after fusion, becomes covered by a black film of protoxide of rhodium. In this compound the rhodium is not attacked by nitric acid. 1 part of rhodium with 4 or 5 of *gold* produces an alloy of the color of gold, very malleable and difficult of fusion, and which becomes covered with a black powder when slowly cooled: 1 of rhodium and 6 of gold forms an alloy more fusible than the former, but less fusible than pure gold: in these compounds the rhodium is not acted on by nitric acid. (WOLLASTON.) The extreme hardness and durability of rhodium induced Dr. Wollaston to suggest it for the nibs of metallic pens, a purpose to which it has been successfully applied.

CHARACTERS OF THE SALTS OF RHODIUM. The salts of the sesquioxide of rhodium are mostly red, or occasionally yellow and brown; their taste is astringent; they are easily reducible by hydrogen; the rhodium is thrown down from them in the form of a black powder by iron, zinc, copper, and mercury, but not by silver; with tin and protochloride of tin they yield brown or yellow precipitates, or are merely discolored, according to their state of dilution; sulphuretted hydrogen occasions a brown precipitate, which, unless aided by heat, is some time in appearing; it is soluble in hydrochloric acid: caustic and carbonated ammonia gradually throw down a yellow precipitate, (of oxide of rhodium and ammonia,) which gives a yellow solution in hydrochloric acid: potassa, and carbonate of potassa, produce no precipitate till the mixed solutions are evaporated, when a brown gelatinous hydrated oxide, combined with potassa, falls. A pure hydrated oxide of rhodium, of a red-brown color, is thrown down by lime-water, from a solution of the sesquioxide of rhodium in hydrochloric acid. The solutions of rhodium are darkened by iodide of potassium, and after some time a scanty precipitate falls: they are not precipitated by phosphate of soda, sal-ammoniac, chloride of potassium, chromate of potassa, oxalic acid, cyanide of potassium or of mercury, ferrocyanides of potassium, or gallic acid. (L. GMELIN.)

§ XXXVI. OSMIUM. Os. 100.

OSMIUM and Iridium are contained in the black powder which remains after the action of nitrohydrochloric acid upon the ore of platinum. This residue, when fused with potassa and washed, furnishes a yellow alkaline solution of oxide of osmium. Saturate the alkali with sulphuric acid, pour the mixture into a retort, and distil: a colorless solution of the *oxide of osmium* passes into the receiver, from which almost all the other metals throw down metallic osmium. (TENNANT, *Phil. Trans.*, 1804; WOLLASTON, *Ibid.*, 1829. See also FREMY *on the Preparation of Osmium and Iridium. Ann. Ch. et Ph.*, Dec. 1844, 512.) To obtain the oxide of osmium in a pure, solid, and crystallized state, grind together, and introduce, when ground, into a cold crucible, three parts by weight of the insoluble powder, and one part of nitre. The crucible is to be heated to a good red in an open fire, until the ingredients are reduced to a pasty state, when osmic fumes will be found to arise from it. The soluble parts of the mixture are then to be dissolved in the smallest quantity of water necessary for the purpose, and the liquor thus obtained is to be mixed in a retort, with so much sulphuric acid, diluted with its weight of water, as is equivalent to the potassa contained in the nitre employed: but no inconvenience will result from using an excess of sulphuric acid. By distilling rapidly into a clean receiver, for so long a time as the osmic fumes continue to come over, the oxide will be collected in the form of a white crust on the sides of the receiver, and there melting, it will run down in drops beneath the watery solution forming a fluid flattened globule at the bottom. When the receiver has become quite cold, the oxide will become solid and crystalline. One such operation has yielded 30 grains of the crystallized oxide, besides a strong aqueous solution of it. This may be agitated with mercury, and the product washed with hydro-

chloric acid to remove the oxide of mercury which is formed. The osmium remains in the form of a black powder, which acquires a metallic lustre by friction. In its densest state, its specific gravity, according to Berzelius, is 10. (*Ann. Ch. et Ph.*, XL. and XLii.)

When osmium is heated in the air it burns into an oxide, and in its pulverulent state it is attacked by nitric acid; but after exposure to a red-heat in close vessels, it becomes much less oxidable. Osmium is extremely poisonous, and has an extraordinary influence upon the brain and nervous system; so that persons have been rendered delirious by inhaling osmic fumes. The equivalent of osmium appears, on the authority of Berzelius, to be about 100, (99·7 TURNER,) and he conceives it susceptible of five degrees of oxidizement.

PROTOXIDE OF OSMIUM. OsO , is obtained by the action of pure alkalis on the protochloride of osmium, or upon the osmio-chloride of potassium: it gradually falls in the form of a nearly black *hydrate*, obstinately retaining a portion of alkali; it dissolves slowly in the acids, forming deep-green or greenish-brown solutions. When heated in a close vessel it gives off water, but does not sublime. It detonates when heated with combustibles. It is reduced by hydrogen with the evolution of heat: its components are

						Berzelius.
Osmium	1	100	92·59 92·56
Oxygen	1	8	7·41 7·44
<hr/>						
Protoxide of osmium....	1		108		100·00	100·00

SESQUIOXIDE OF OSMIUM. Os_2O_3 , has not been obtained in an insulated state, but is produced in combination with ammonia when the peroxide is heated with excess of ammonia, nitrogen being at the same time evolved. On evaporating the ammoniacal solution a black powder falls, which becomes brown when dried, and is a hydrated compound of the sesquioxide with ammonia: when heated it deflagrates and is reduced: after having been boiled with caustic potassa it is explosive: it is sparingly soluble in acids, forming brown solutions: it dissolves in caustic and carbonated alkalis without loss of ammonia, and when precipitated by an alkali from its acid solutions it still retains ammonia: these solutions are not precipitated by zinc or iron. (BERZELIUS.) The composition of this oxide is

						Berzelius.
Osmium!.....	2	200	89·29 89·24
Oxygen	3	24	10·71 10·76
<hr/>						
Sesquioxide of osmium.....	1		224		100·00	100·00

BINOXIDE OF OSMIUM. OsO_2 . When a saturated solution of bichloride of osmium, or of the osmio-bichloride of potassium, is heated with carbonate of soda, the binoxide gradually falls; it retains a little alkali, which may be removed by dilute hydrochloric acid; if it then be washed and dried at 212° , it only retains water, which it gives off when more highly heated, and remains anhydrous. In this state it appears insoluble in the acids, but it is a salifiable base when in its nascent state. It consists of

						Berzelius.
Osmium	1	100	86.3 86.15
Oxygen	2	16	13.7 13.85
<hr/>						<hr/>
Binoxide of osmium	1		116		100.0	100.00

TEROXIDE OF OSMIUM. OsO_3 , is assumed, by Berzelius, to exist in certain salts of this metal, but it has not been isolated.

PEROXIDE OF OSMIUM. OSMIC ACID. OsO_4 . This is the volatile oxide above adverted to, and is obtained by the combustion of the metal in oxygen, or by the action of boiling nitric acid, or by the fusion of osmium with nitre or with potassa. When osmium is heated, and a current of oxygen passed over it, white or yellowish crystals of the anhydrous peroxide are formed: these dissolve slowly in water, and readily in alcohol and ether; the solutions gradually deposit metallic osmium. Other combustibles deoxidize it; by sulphurous acid its solution is rendered yellow, orange, brown, green, and lastly blue, colors corresponding to different degrees of oxidizement. It stains the skin. It may be volatilized in hydrogen gas, but when its vapor and hydrogen are passed through a red-hot tube, it is reduced. It is reduced by sulphuretted hydrogen, and sulphuret of osmium is formed. The odor of the vapor of this oxide is very peculiar; it has been by some compared to that of chlorine; it is acrid, and poisonous; when much diluted, it a little resembles the smell of new wheaten bread; this is the origin of the term *osmium*, from $\delta\sigma\mu\eta$, *odor*. It has no acid reaction, but as it combines with alkalis, and forms compounds which are permanent at high temperatures, it has sometimes been termed *osmic acid*. When infusion of galls is dropped into its aqueous solution, a very characteristic blue color is produced, which Berzelius ascribes to a mixture of the peroxide and sesquioxide. Its components are

						Berzelius.
Osmium	1	100	75.75 75.672
Oxygen	4	32	24.25 24.328
<hr/>						<hr/>
Osmic acid	1		132		100.00	100.000

CHLORIDES OF OSMIUM. Berzelius has described four chlorides of this metal, corresponding in composition to the oxides. When chlorine is transmitted over heated osmium, a beautiful dark-green sublimate of *protochloride of osmium* is the result. This is succeeded by a red sublimate, which is the *bichloride*. The *sesquichloride* and *perchloride* have not been obtained in a separate state; Berzelius infers their existence in combination with sal-ammoniac, in certain *osmio-chlorides* of ammonium: he has also examined the double salts, produced by the union of protochloride and perchloride of osmium with the chloride of potassium. When osmic acid is dissolved in hydrochloric acid, or when osmium is digested in nitrohydrochloric acid, an orange-colored solution is obtained, which is at first rendered blue by the immersion of a plate of zinc, and afterwards metallic osmium falls as a black powder: when this solution is diluted it is rendered blue by tincture of galls. (VAUQUELIN.)

SULPHURETS OF OSMIUM. Sulphur and osmium apparently combine,

in several proportions, for sulphuretted hydrogen precipitates it from all its solutions.

The remaining compounds of this remarkable metal have not been sufficiently examined, to enable us to give satisfactory details respecting them. A few of its *alloys* have been noticed by Tennant, and the characters of its salts will be sufficiently obvious from the preceding statements. The best details upon the subject of osmium and its compounds, will be found in Berzelius' *Lehrbuch*, and in L. Gmelin's *Handbuch der Chemie*.

§ XXXVII. IRIDIUM. Ir. 99.

THIS metal was discovered by Tennant in 1803, and about the same time by Descotils: the various colors exhibited by the hydrochloric solution of its oxide suggested its name (from *Iris*, the rainbow). The black powder which remains after native platinum has been digested in nitrohydrochloric acid, consists chiefly of iridium and osmium; titanium and chromate of iron also occur in it. To obtain iridium, this powder is fused in a silver crucible, with twice its weight of hydrate of potassa, for the space of an hour or more; the residue is washed, by which, as already stated, the oxide of osmium is removed, and the remaining insoluble portion is *iridium*, which has been partially oxidized by the process of fusion. This oxide is soluble in hydrochloric acid, and the solution is blue, if free from iron, which communicates more or less of a green tint: when heated with the addition of a little nitric acid, it becomes red, probably in consequence of the peroxidizement of the iridium. When the hydrochloric solution of iridium is evaporated, it furnishes brown crystals, which are decomposed by a red heat, and leave finely-divided metallic iridium. They form a reddish-brown solution with water, which if concentrated and mixed with a saturated solution of sal-ammoniac, afford a dark-brown precipitate of the *ammonio-chloride of iridium*. The solution of the chloride is decomposed by all the metals except gold and platinum, and metallic iridium precipitated.

Iridium, obtained by immersing a plate of zinc into a solution of the chloride, or by violently heating that salt, is of a whitish color, and, according to Children, who succeeded in fusing it by means of his large Voltaic apparatus, its specific gravity is about 18. The approximate specific heat of iridium is, according to Regnault, $=0.03683$. Its most marked character is extremely difficult solubility in the acids: indeed, when pure, it is probably insoluble, although, when alloyed with platinum, a little is taken up by nitrohydrochloric acid. Its equivalent may be assumed as about 99.

OXIDES OF IRIDIUM. According to Berzelius there are four oxides of iridium, separable from the corresponding *chlorides* by the action of alkalis.

PROTOXIDE OF IRIDIUM. IrO , is obtained by decomposing the protochloride by a solution of caustic potassa; the product is to be washed with dilute acid, and afterwards with water, and dried; it is a heavy black powder, which loses oxygen at a red-heat; it is not soluble in the acids, but with potassa yields a blue or purple solution. The hydrate of this

oxide is thrown down in the form of a greenish-grey powder, when the iridiochloride of potassium, KCl, IrCl , is decomposed by carbonate of potassa. This oxide consists of

Iridium	1	99	92.52
Oxygen	1	8	7.48
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Protoxide of iridium	1		107		100.00

SESQUIOXIDE OF IRIDIUM. Ir_2O_3 , is formed when iridium is calcined with nitre or caustic potassa; or by exposing a mixture of the iridiobichloride of potassium, KCl, IrCl_2 , with twice its weight of carbonate of potassa, to a dull red-heat; the residue when washed leaves this oxide in the form of a black powder; it requires a very high red-heat for its decomposition; hydrogen gas decomposes it at common temperatures, in consequence probably of an action similar to that of spongy platinum. The hydrate of this sesquioxide is obtained in the form of a bulky dark reddish-brown precipitate, when a solution of the sesquichloride, or one of its double salts, is decomposed by an alkali; if ammonia be used, the precipitate deflagrates when heated. The saturated alkaline solutions of this sesquioxide are decomposed when diluted with water; its hydrate combines with acids, but when anhydrous it is insoluble in them. The components of this oxide are

Iridium	2	198	89.19
Oxygen	3	24	10.81
<hr/>					
Sesquioxide of iridium	1		222		100.00

BINOXIDE OF IRIDIUM. IrO_2 , has not been isolated, but it exists in a class of salts, and appears to be soluble in the alkalis and their carbonates.

PEROXIDE OF IRIDIUM. IrO_3 . Berzelius describes this under the name of *sesquioxide*, but represents it by IrO_3 , and states that it contains between 19 and 20 *per cent.* of oxygen. To obtain it he heats the purest osmic iridium to redness, with nitre, and digests the residue in nitrohydrochloric acid; then expels the osmic acid and excess of nitric acid, by heat, evaporates to dryness, and dissolves the remaining saline mass in water to separate it from the insoluble matter: this solution is then evaporated and the remaining salt acted on by a little water, which at first forms a colorless solution of chloride of potassium; a second portion of water then yields a red solution, and by the alternate action of small quantities of water, rose-colored and reddish-yellow solutions are obtained. In these operations two double iridiopotassium salts are formed, which are both insoluble in a saturated solution of chloride of potassium. But one of these salts, namely, that which gives a rose-colored solution, is soluble in a dilute solution of chloride of potassium, in which the other is almost insoluble: this last insoluble salt, which constitutes the principal part of the product, is the iridiochloride of potassium; the other is the iridioperchloride: when the solution of the latter is mixed with carbonate of potassa or soda, it is rendered slightly turbid, but on the application of heat a brownish gelatinous hydrate falls, exactly resembling that from the double rhodium salt: after having been well washed, it still retains alkali; when dried and heated in a retort it decre-

pitates and loses water and part of its oxygen : the relations of this oxide to the oxyacids have not been determined; with hydrochloric acid it forms a yellow solution, which acquires a red color when evaporated nearly to dryness : this oxide consists of

						Berzelius.
Iridium	1	99	80.49 80.435
Oxygen	3	24	19.51 19.565
<hr/>						<hr/>
Peroxide of iridium	1		123		100.00	100.000

PROTOCHLORIDE OF IRIDIUM. IrCl , is formed by the action of chlorine on pulverulent iridium heated to incipient redness; it is a dark-olive powder : it is decomposed at a high heat, giving off chlorine and sesquichloride, and leaving iridium ; it is insoluble in water; very slightly soluble in boiling hydrochloric acid, and scarcely affected by nitrohydrochloric acid; it is resolved by excess of potassa into chloride of potassium and protoxide of iridium; it forms double iridio-protochlorides. Its components are

						Fellenberg.
Iridium	1	99	74.08 73.78
Chlorine	1	36	25.92 26.22
<hr/>						<hr/>
Protochloride of iridium	1		135		100.0	100.00

SESQUICHLORIDE OF IRIDIUM. Ir_2Cl_3 . When iridium is calcined with potassa and nitre, and the resulting product supersaturated by nitric acid, an oxide is obtained, which when washed, and dissolved in hydrochloric acid, yields chloride and sesquichloride of iridium; the latter forms a brown solution, which, evaporated to dryness and digested in alcohol, gives a solution of sesquichloride, and a residue of the double iridiochloride of potassium. The sesquichloride is obtained on evaporating the alcoholic solution, in the form of a deliquescent uncrystallizable compound of a black hue; it tinges water deep-brown; it is always hydrated, and, when heated, gives off hydrochloric acid, and forms an oxichloride which is decomposed at a higher heat. This chloride forms double salts with the alkaline chlorides: their solutions are deep brown, and, when boiled with excess of alkaline chloride, are decomposed, the sesquichloride of iridium becoming protochloride and bichloride, and forming two double salts, of which those of the protochloride are dissolved, and those of the bichloride deposited. The sesquichloride consists of

Iridium.....	2	198	64.71
Chlorine	3	108	35.29
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Sesquichloride of iridium....	1		306		100.00

BICHLORIDE OF IRIDIUM, IrCl_2 , is obtained by calcining iridium with nitre and potassa, washing the resulting oxide, dissolving it in nitrohydrochloric acid, and evaporating to dryness; the bichloride remains nearly pure; at a high heat, it gives out water and hydrochloric acid, and produces oxide of iridium; its aqueous solution is deep red; it is soluble in alcohol, but this solution decomposes spontaneously into hydrochloric acid, sesquichloride, and iridium. Bichloride of iridium consists of

Iridium	1	99	57·9
Chlorine	2	72	42·1
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Bichloride of iridium	1		171		100·0

IRIDIO-BICHLORIDES. The bichloride of iridium produces characteristic double salts. When an intimate mixture of metallic iridium and chloride of potassium is heated, and subjected to the action of a current of chlorine, the *iridio-bichloride of potassium*, KCl, IrCl_2 , is formed; the resulting product should be washed in water acidulated by nitro-hydrochloric acid, the undissolved iridium separated by deposition, and the solution evaporated to dryness; the excess of chloride of potassium may then be removed by water, for the double chloride is insoluble in the solution of that salt. Thus purified, the double salt may be again dissolved in the acidulated water, and obtained, by due evaporation, in anhydrous octohedral crystals. This salt is black in mass, but red in powder; it is insoluble in alcohol, which throws down a brown or deep red precipitate from its solutions; it is not fusible, nor decomposed at a dull red-heat; a higher temperature converts it into sesquichloride, and an intense heat into chlorine and metallic iridium, which remains mixed with chloride of potassium. *Iridio-bichloride of sodium*, NaCl, IrCl_2 , is prepared as the preceding, and has the same general properties, but it includes water of crystallization, and forms tabular, or quadrangular prismatic crystals with dihedral summits, $= \text{NaCl, IrCl}_2, 6\text{HO}$. When a solution of *bichloride of iridium* is mixed with one of *sal-ammoniac*, a double salt is obtained, little soluble in water, and insoluble in alcohol, and which, when heated, leaves pure iridium; it is of so deep red a color as to appear almost black, and the slightest traces of it give a red tinge to the ammonio-chloride of platinum; 1 part dissolved in 20 of water form a very deep orange-colored solution; indeed, according to Vauquelin, its coloring power is so great, that 1 part of it gives a decided tint to 40,000 of water. Ammonia decolors this solution without producing a precipitate; protosulphate of iron, sulphuretted hydrogen, and zinc, iron, and tin produce the same effect, and chlorine restores the color. This double salt consists of

Bichloride of iridium	1	171	76
Chloride of ammonium.....	1	54	24
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Ammonio-bichloride of iridium	1		225		100

SULPHURETS OF IRIDIUM. When the respective chlorides of iridium are decomposed by sulphuretted hydrogen, a series of sulphurets corresponding with the chlorides appear to be formed; they are of a deep brown, and resemble the sulphurets of platinum, rhodium, and palladium: they are soluble in potassa and in carbonate of potassa, and in alkaline sulphurets. When equal parts of sulphur and of the preceding ammonio-bichloride are heated together, a bisulphuret is obtained, composed of

Iridium	1	99	75·57
Sulphur	2	32	24·43
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Bisulphuret of iridium	1		131		100·00

SULPHATES OF IRIDIUM. When the sulphurets prepared by precipitation are digested, whilst moist, in cold nitric acid, they are converted into sulphates of iridium, the solutions of which are dark-green, brown, or orange, according as they contain the protoxide, sesquioxide, or binoxide.

PHOSPHURET OF IRIDIUM is obtained by heating the metal in the vapor of phosphorus; a compound resembling iridium in appearance is formed, which burns, when heated red-hot, in the air, and is converted into iridium, and phosphate of oxide of iridium.

CARBURET OF IRIDIUM. When iridium is immersed in the flame of alcohol, black excrescences of carburet form upon it, which, burned in the air, leave pure iridium, so that, as soon as it is formed by the above process, it must be immediately dropped into water on withdrawing it from the flame; its composition appears to be

						Berzelius.	
Iridium	1	...	99	...	80.49	...	80.2
Carbon.....	4	...	24	...	19.51	...	19.8
<hr/>						<hr/>	
Carburet of iridium	1		123		100.00		100.0

ALLOYS OF IRIDIUM. These require a very high heat for their formation; the ductile metals may be combined with a considerable proportion of iridium without loss of ductility. The greater number of these alloys, when digested in nitric acid, leave a pulverulent residue of iridium; nitrohydrochloric acid dissolves them when the proportion of iridium is not very considerable. The *native alloy of iridium and osmium* forms small crystals of much lustre, harder than steel, and as refractory as iridium; they fuse, however, as well as iridium, in the arc of flame between the charcoal points of a powerful voltaic battery. (DANIELL.) The density of these grains is 18.64.

In consequence of the extreme infusibility of iridium, and of the native alloy of iridium and osmium, grains of these substances are sometimes diffused through the ingots of gold which are cast from the native gold of those parts of America and Asia whence platinum and its associates are derived; and as at the temperature at which gold fuses these grains have no tendency to combine with that metal, they remain diffused through it after a number of successive fusions, but are generally in such small quantity as to elude observation. In our coined gold monies, however, it occasionally happens that one or more of these grains of the white metal may be discerned; and where very large quantities of gold are melted, if there be any of these grains present, they will have a tendency, in consequence of their specific gravity as compared with *standard* gold (being as about 18 to 17), to sink to the bottom of the crucible, so that in great gold coinages at the Mint it has occasionally happened that several ounces of the ore of iridium have been thus accumulated.

SALTS OF IRIDIUM. These salts have not been minutely examined; those obtained by dissolving the hydrated protoxide are generally green and uncrystallizable. The sulphate of the binoxide of iridium is yellow, uncrystallizable, and soluble in water and alcohol, forming an orange-

colored solution not precipitated by the alkalis, but which gives, with chloride of barium, a precipitate of sulphate of baryta, colored brown by the binoxide.

§ XXXVIII. GLUCINUM. G. 5.

GLUCINUM, GLYCIUM, or BERILLIUM, was first obtained in 1828, by Wöhler, by the action of potassium on *chloride of glucinum*. Flattened globules of potassium are stratified with alternating layers of chloride of glucinum in a small platinum crucible the cover of which is bound on by wire; it is then heated over a spirit-lamp, when a sudden and violent action ensues, attended by the evolution of so much heat as to render the crucible white-hot. Sodium effects the decomposition as well as potassium, and is cheaper, but in either case care should be taken to use as far as possible equivalent proportions; at all events the alkaline metal should not prevail. When the crucible has become cold, the cover is removed, and it is put into a glass of water, which dissolves the fused chloride of potassium or sodium, and leaves the glucinum in a pulverulent form, so that it may be collected upon a filter, washed, and dried. Thus obtained, glucinum is a grey substance, having a slight metallic lustre, and very difficult of fusion. At common temperatures it is not acted on by air or water, but when heated in the air it burns into glucina: it burns vividly in oxygen gas, in chlorine, and in the vapor of iodine and bromine. It combines, with the evolution of heat and light, with sulphur, phosphorus, selenium, and arsenic. (WÖHLER, *Ann. Ch. et Ph.*, 1828.) The equivalent of glucinum deduced from the researches of Awdejew (*Poggend.*, lvi. 101; *Phil. Mag.*, October, 1842), is as low as 4.647; Gmelin adopts the number 4.7. I have assumed 5 as the atomic weight of this metal, which very closely approximates to the analyses which will be quoted.

OXIDE OF GLUCINUM, or GLUCINA, GO , was discovered in 1798, by Vauquelin, in the *beryl*: it also exists in the *emerald* of Peru, in *euclase*, in the *chrysoberyl*, in *phenakite*, and in a few other rare minerals. It is white, insipid, and insoluble in water; it has no action on vegetable colors; its specific gravity is 2.97. It dissolves, especially in the state of hydrate, in solution of caustic potassa and soda, but not in ammonia, and thus resembles alumina, but differs from yttria. Again it differs from alumina, but resembles yttria, in being soluble, when freshly precipitated, in carbonate of ammonia; it is much more soluble in this solution than yttria. With the acids it forms saline compounds of a sweetish astringent taste, (hence the name, from $\gamma\lambda\upsilon\kappa\upsilon\varsigma$, *sweet*.) From these solutions the carbonates of potassa and soda throw it down in the form of a bulky hydrated carbonate, soluble in great excess of those precipitants. Common phosphate of soda occasions a white flocculent precipitate in solutions of the salts of glucina; ferrocyanide of potassium at first produces no turbidness, but after a time the mixture becomes gelatinous. These salts are not precipitated by sulphuretted hydrogen, nor by oxalates, or tartrates.

i. The *beryl*, or *aquamarine*, is found in primitive rocks in many

parts of the world, but especially fine in Siberia. It is usually transparent, and pale-green or blue. It crystallizes in six-sided prisms. ii. The *emerald* is principally found in Peru, crystallized in regular six-sided prisms, the edges or angles of which are sometimes replaced by facets. Its color is green, and it is either transparent or translucent. iii. *Euclase* is a very rare crystallized mineral, originally found in Peru, but has since been brought, in insulated crystals, from the Brazils. iv. *Chrysoberyl*, or *Cymophane*, occurs most frequently in Brazil, where it accompanies topazes in alluvial soil; it has also been found in Ceylon, and in Siberia; it is green, or yellow-green, and in one direction slightly opalescent; it occurs in rounded pieces and prismatic crystals. Specific gravity 3·7. v. *Phenakite*. This mineral was discovered by Nordenskiöld mixed with emerald from the Uralian Mountains; it had been mistaken for quartz, hence the above name, from *φεναξ*, *deceiver*; it forms flat colorless rhomboids.

These minerals, analyzed by Vauquelin, Thomson, and Hartwall, are constituted as follows:

	Beryl. Vauquelin.)	Emerald. (Vauquelin.)	Euclase. (Vauquelin.)	Chrysoberyl. (Thomson.)	Phenakite. (Hartwall.)
Silica	68	64·5	44·33	—	55·14
Alumina	15	16·0	31·83	76·75	—
Glucina	14	13·0	23·84	17·79	44·47
Oxide of chromium	—	3·0	—	—	—
Oxide of iron	1	—	—	4·50	—
Lime	2	1·5	—	—	—
Water and loss ...	—	2·0	—	0·96	0·39
	100	100·0	100·00	100·00	100·00

To obtain glucina from either of these minerals, proceed as follows: reduce it to a fine powder, and fuse it in a platinum crucible with thrice its weight of carbonate of potassa; dissolve the fused mass in dilute hydrochloric acid, and evaporate to dryness, by which the silica is rendered insoluble: digest this dry residue in water acidulated by hydrochloric acid, and add ammonia, which throws down a mixture of glucina and alumina; wash the precipitate, and digest it whilst moist in excess of solution of carbonate of ammonia, (of which a large quantity is requisite), by which the glucina is dissolved, and, on filtering, the alumina remains behind; then boil the filtered liquid, and carbonate of glucina is thrown down, which, washed, dried, and heated to redness, affords pure glucina. Berthier has suggested the following modification of this process: he washes the mixed precipitate with ammonia and dissolves it in a cold solution of caustic potassa, which leaves any oxide of iron that may be present; the potassa solution is then saturated by hydrochloric acid and precipitated by caustic ammonia: this precipitate is then washed and diffused in water through which sulphurous acid gas is passed till the whole is redissolved; the sulphurous acid is then expelled by boiling, during which basic sulphite of alumina falls in the form of a dense powder which is easily separable; the glucina remains dissolved and may be precipitated by ammonia. Glucina consists of

				Awdejew.	Berzelius.
Glucinum.....	1	5	38·46	37·01	36·74
Oxygen	1	8	61·54	62·99	63·26
Glucina	1	13	100·00	100·00	100·00

Hydrated Glucina falls on adding an alkali to a soluble salt of glucina; when obtained by the decomposition of a solution of chloride of glucinum by ammonia it resembles hydrate of alumina, but it falls on drying into a white powder, which, when dried at 212° , retains, according to Schaffgotsch, between 48 and 49 *per cent.* of water; it is therefore considered as $= 3\text{GO}, 4\text{HO}$.

CHLORIDE OF GLUCINUM. GCl . When glucinum is gently heated in chlorine it burns vividly and a crystallized chloride sublimes. When a stream of chlorine is passed through a porcelain or glass tube containing a mixture of glucina and carbon at a red heat, this chloride is also formed; it produces silky flakes and needles, or a fused crystalline mass. It has already been adverted to as the only source of its metallic base. It is extremely deliquescent, and rapidly soluble in water with evolution of heat. This solution, or glucina dissolved in hydrochloric acid, yields crystals which are $\text{GCl} + 4\text{HO}$. (AWDEJEW.) When heated they lose water and leave glucina. Chloride of glucinum consists of

						Awdejew.
Glucinum	1	5	12.19 11.74
Chlorine	1	36	87.81 88.26
<hr/>						
Chloride of glucinum	1		41		100.00	100.00

IODIDE OF GLUCINUM. GI . Glucinum burns when heated in the vapor of iodine, and produces a white acicular sublimate, fusible and very volatile, and which evolves heat when dissolved in water. (WÖHLER.)

BROMIDE OF GLUCINUM. When glucinum is heated in bromine vapor it produces a very volatile compound, which condenses in white fusible acicular crystals which evolve much heat on solution in water. (WÖHLER.) A solution of glucina in hydrobromic acid yields small cubic crystals, extremely deliquescent, and which give out bromine vapor when heated. (BERTHEMOT, *Ann. Ch. et Ph.*, XLIV. 394.)

FLUORIDE OF GLUCINUM. The solution of glucina in hydrofluoric acid leaves a gumlike residue on evaporation, which, at 212° becomes milk-white, and loses water; at a red-heat it swells up like alum, and begins to evolve acid: its aqueous solution is less sweet than the other glucinum salts, and it forms double salts with the alkalis. (BERZELIUS.) Mixed with fluoride of potassium it affords on evaporation small anhydrous and difficultly soluble crystals $= \text{KF}, \text{GF}$. (AWDEJEW.)

NITRATE OF GLUCINA is not crystallizable, it is very deliquescent, and soluble in alcohol. (VAUQUELIN.)

SULPHURET OF GLUCINUM. Glucinum burns brilliantly in sulphur vapor, forming a grey compound difficultly soluble in water, and evolving sulphuretted hydrogen with acids. (WÖHLER.)

SULPHITE OF GLUCINA. Glucina dissolves in aqueous sulphurous acid, and affords no precipitate when the solution is boiled: this is distinctive between it and alumina. (BERTHIER, *Ann. Ch. et Ph.*, L. 371.)

SULPHATE OF GLUCINA. GO, SO_3 . When glucina is dissolved in excess of sulphuric acid, evaporated till acid begins to escape, and then alcohol added, a crystalline powder separates, the solution of which in hot water deposits octohedral crystals $= \text{GO}, \text{SO}_3, 4\text{HO}$; at a red-heat they lose water and acid and leave pure, but difficultly soluble glucina. The aqueous solution of this sulphate dissolves recently precipitated carbonate of glucina, and deposits a *subsulphate*, being, according to Awdejew, $= 6\text{GO}, \text{SO}_3, 3\text{HO}$; after evaporation to dryness the residue is separated by the action of water into an insoluble tribasic, and a soluble bibasic sulphate. (BERZELIUS. AWDEJEW.)

PHOSPHURET OF GLUCINUM. Glucinum burns in the vapor of phosphorus as in that of sulphur, and produces a grey pulverulent phosphuret, which disengages phosphuretted hydrogen in water. (WÖHLER.)

HYPOPHOSPHITE OF GLUCINA remains in the form of an uncrystallizable gumlike mass on evaporating in vacuo a saturated solution of hydrated glucina in cold hypophosphorous acid. (H. ROSE, *Poggend.*, xii. 86.)

PHOSPHITE OF GLUCINA. Phosphite of ammonia gives a white precipitate with a solution of chloride of glucinum: when dried and heated in a retort, it evolves hydrogen, and becomes incandescent. (H. ROSE, *Poggend.*, ix. 40.)

PHOSPHATE OF GLUCINA is precipitated in a gelatinous form when phosphate of soda is added to solution of chloride of glucinum: it fuses into a transparent glass: it is insoluble in water, but soluble in dilute acids. (VAUQUELIN.)

SELENIURET OF GLUCINUM is formed as the sulphuret, and with the same phenomena: it is a grey crystalline compound. (WÖHLER.)

SELENITE OF GLUCINA is a white insoluble powder: the *biselenite* is soluble and uncrystallizable. (BERZELIUS.)

CARBONATE OF GLUCINA falls in the form of a bulky flocculent precipitate, which is light and soft when dried; it is easily decomposed by heat. It is not sensibly soluble in aqueous carbonic acid, but soluble in solutions of the carbonated alkalis. According to Vauquelin hydrated glucina attracts carbonic acid from the atmosphere. The formula of the above precipitate given by Schaffgotsch is $5\text{GO}, \text{CO}_2, 5\text{HO}$.

CHARACTERS OF THE SALTS OF GLUCINA. These salts are astringent and sweet: they are precipitated by the caustic fixed alkalis, and the precipitate is redissolved by their excess, and sparingly by their carbonates: it is not soluble in caustic ammonia, but readily so in carbonate of ammonia. A characteristic property of glucina is, that when a warm solution is mixed with a warm solution of fluoride of potassium till a precipitate begins to appear, and the mixture then suffered to cool, a difficultly-soluble double salt separates in the form of lamellar crystals. (BERZELIUS.) Sulphate of glucina does not form a crystallizable double salt when mixed with sulphate of potassa.

§ XXXIX. ZIRCONIUM. Zr. 23.

SIR H. DAVY first demonstrated the nature of *Zirconia*, and its metallic base was obtained by Berzelius in 1824 by acting upon the potassio-fluoride of zirconium by potassium: he proceeded as follows; the potassio-fluoride was well dried and introduced in alternating portions with the potassium into an iron or glass tube; this was then heated so as to fuse its contents which were stirred together by a steel wire, and then the temperature was raised to redness; under these circumstances fluoride of potassium is produced and zirconium set free, the reduction taking place without noise or explosion: when cold the product is thrown into water, and the zirconium separates in the form of a black powder, having the appearance of plumbago, and not apparently conducting electricity. It is difficultly-soluble in the acids, with the exception of the hydrofluoric, which readily dissolves it, evolving hydrogen. Heated in the atmosphere, it burns into zirconia. Its equivalent, deduced from the analyses of Berzelius, is about 23, if zirconia be regarded as a protoxide. (22·4 GMELIN; 33·67 GRAHAM, who, however, assumes Zirconia to be Zr_2O_3 .)

OXIDE OF ZIRCONIUM. ZIRCONIA. ZrO , was discovered in 1789 by Klaproth: it is of rare occurrence, having only been found in the *Zircon* or *Jargon* (whence the name of this earth) and in *Eudialite*, which are *silicates of zirconia*; in *Æschynite* and *polymignite*, which contain *titanate of zirconia*; and in *Sillimanite*, which is a *silicate of alumina and zirconia*. The zircon is found in Ceylon, and occurs in some sienitic rocks: when colorless and transparent, it ranks among the gems: when colored brown or red, it is termed *hyacinth* or *jacinth*, which also occurs in Ceylon, and is found in small crystals in the sand of the rivers of that island; also near Pisa in Italy; in Brazil; and abundantly in the sands of the brook of Expailly in France (Dép. Haute Loire). This mineral contains between 60 and 70 *per cent.* of zirconia combined with silica and a little oxide of iron. Zirconia is obtained by the following processes: (1) Reduce the colorless zircons to a fine powder, having previously heated them to redness, and quenched them in water. Mix the powder with nine times its weight of hydrated potassa, and gradually project it into a red-hot silver crucible, and keep it in perfect fusion for two hours. When the crucible has cooled, reduce the mass to a fine powder, and boil it in distilled water. Boil the undissolved residue in hydrochloric acid; filter, and evaporate to dryness; redissolve the dry mass in distilled water, and precipitate by carbonate of soda. The carbonate of zirconia which falls may be decomposed by heat. (KLAPROTH.) (2) The following method of obtaining pure zirconia is recommended by Dubois and Silveira. (*Ann. de Ch. et Ph.*, xiv. 110.) Powder the zircons very fine, mix them with 2 parts of hydrated potassa, and heat them red-hot in a silver crucible for an hour. Treat the substance obtained with distilled water, pour it on a filter, and wash the insoluble part well; it will be a compound of zirconia, silica, potassa, and oxide of iron. Dissolve it in hydrochloric acid, and evaporate to dryness, to separate the

silica. Redissolve the salts of zirconia, potassa, and iron in water; and to separate the zirconia which adheres to the silica, wash it with weak hydrochloric acid, and add the washings to the solution. Filter the fluid, and precipitate the zirconia and iron by pure ammonia; wash the precipitate and treat it with a boiling solution of oxalic acid, which retains the iron, whilst an insoluble oxalate of zirconia is formed. Filter, and wash the remaining oxalate till no iron can be detected in the washings. The oxalate of zirconia, when dry, is of an opaline color; after being well washed, it is to be decomposed by heat in a platinum crucible. Thus obtained, the zirconia is perfectly pure, but is not affected by acids. It must be re-acted on by potassa as before, and then washed until the alkali is removed. Afterwards dissolve it in hydrochloric acid, and precipitate by ammonia. The hydrate thrown down, when well washed, is perfectly pure, and easily soluble in acids. (3) According to Wöhler, zirconia is best obtained as follows: 1 part of finely pulverized zircons is mixed with 4 parts of anhydrous carbonate of soda and put into a platinum crucible, which is placed in an earthen crucible with a little magnesia between them, by which any injury to the platinum is prevented: the crucibles thus arranged, and covered, are heated to whiteness for half an hour in a wind-furnace, when the contents of the platinum crucible are fused: on cooling, water is added, which abstracts carbonate and silicate of soda, and leaves a crystalline powder, which, according to Scherer, is a compound of zirconia and soda; this is to be washed and moistened with hydrochloric acid, which decomposes it with heat, and renders it soluble in water; from this solution, ammonia throws down pure hydrated zirconia. (*Berzelius' Lehrbuch*, ii. 184.)

When pure and colorless hyacinths or zircons have been used, and those selected which remain colorless after having been heated red-hot, the zirconia is obtained from them free from iron; but the common zircons and hyacinths yield the earth contaminated by oxide of iron, for the separation of which several especial processes have been suggested. (See BERZELIUS.) Among them the following, by Berthier, may be selected: the solution of ferriferous zirconia is either precipitated by a mixture of ammonia with a little hydrosulphuret of ammonia, or the liquid is first saturated with sulphuretted hydrogen, and then precipitated by ammonia and put into a stopped bottle till clear, taking care that there is sulphuret of ammonium in excess: it is then syphoned or poured off from the black precipitate, which is a mixture of zirconia and sulphuret of iron; this is treated with excess of aqueous sulphurous acid, which immediately dissolves the sulphuret of iron, and leaves the pure and white zirconia: a portion of zirconia is also taken up, which however falls free from iron, on boiling the sulphurous solution: when zirconia is free from iron, it is not discolored by hydrosulphuret of ammonia.

Pure zirconia is a white infusible substance, insoluble in water, specific gravity 4.3: it gives intense luminosity to the blow-pipe flame. After having been heated to redness it scratches glass and resists the action of the acids, with the exception of the sulphuric; according to Berzelius, the best method of rendering it again soluble consists in mixing it in fine powder with sulphuric acid diluted with its weight of water, and heating the whole in a platinum crucible till the excess of acid is evaporated, but not to redness: the *sulphate of zirconia* thus obtained is soluble in hot water.

From this solution, *hydrate of zirconia* is thrown down by caustic ammonia, in the form of a bulky gelatinous precipitate, which if dried, or even washed with boiling water, loses its easy solubility in acids; when exposed to a red-heat it becomes remarkably luminous after it has lost its water: it appears to be sparingly soluble in the alkaline carbonates, and consists of 2 atoms of zirconia and 1 of water. Zirconia is composed of

						Berzelius.
Zirconium	1	...	23	...	74.2	73.69
Oxygen	1	...	8	...	25.8	26.31
<hr/>						<hr/>
Zirconia	1		31		100.0	100.00

CHLORIDE OF ZIRCONIUM, ZrCl_2 , is obtained in the form of a white fixed compound, by heating zirconium in chlorine. (BERZELIUS.) Wöhler obtained chloride of zirconium by passing a stream of chlorine over an intimate mixture of zirconia and carbon, obtained by burning a mixture of zirconia and sugar: it formed a white sublimate: he recommends this as a preliminary process for obtaining zirconia free from silica, for the chloride of silicium goes off in the gaseous form. Hydrated zirconia dissolves readily in hydrochloric acid, and the solution yields, on evaporation, small acicular silky crystals of *hydrated chloride*, soluble in water and in alcohol, but only sparingly soluble in hydrochloric acid. The anhydrous chloride cannot be obtained pure by heating this hydrate, for in that case it loses half its chlorine in the form of hydrochloric acid, whilst half the zirconium becomes zirconia. (BERZELIUS.)

BROMIDE OF ZIRCONIUM. The solution of hydrated zirconia in hydrobromic acid yields with difficulty small granular crystals of a slightly astringent taste: when heated they are resolved into zirconia and hydrobromic acid. (BERTHEMOT, *Ann. Ch. et Ph.*, XLIV. 393.)

FLUORIDE OF ZIRCONIUM. Zirconia dissolves readily in hydrofluoric acid, and yields, by slow evaporation, a crystallized salt, which, by the action of water, is resolved into a basic and an acid salt. When solution of fluoride of potassium is added to excess of fluoride of zirconium, the solution yields, on evaporation, small granular crystals, sparingly soluble in cold water, of *potassiofluoride of zirconium*, consisting, according to Berzelius, of

Potassium	1	...	40	...	27.97
Zirconium	2	...	46	...	32.17
Fluorine.....	3	...	57	...	39.86
<hr/>					
Potassiofluoride of zirconium	1		143		100.00

When solution of fluoride of zirconium is dropped into excess of fluoride of potassium, an analogous triple compound is formed, containing 2 atoms of potassium, 3 of zirconium, and 5 of fluorine. (BERZELIUS.)

NITRATE OF ZIRCONIA is a very soluble and uncrystallizable compound: its solution dissolves hydrate of zirconia, and it is only imperfectly decomposed by the addition of alkalis.

SULPHURET OF ZIRCONIUM is formed by heating sulphur and zirconium in an exhausted vessel, or in an atmosphere of hydrogen; in the latter case light is emitted, and a pulverulent brown sulphuret formed. It is insoluble in nitric, hydrochloric, and sulphuric acid, feebly acted on by nitrohydrochloric acid, but dissolved and decomposed by hydrofluoric acid. (BERZELIUS.)

SULPHITE OF ZIRCONIA falls as a basic salt when solutions of sulphite of ammonia and chloride of zirconium are mixed: the precipitate is soluble in excess of sulphite of ammonia, and this solution is not precipitated by potassa: when the solution of the ammonio-sulphite is boiled, hydrated zirconia falls. (BERTHIER. BERZELIUS.)

SULPHATE OF ZIRCONIA. ZrO,SO_3 . This salt is formed by digesting zirconia with sulphuric acid and a little water; the mixture must be boiled to dryness, and ultimately heated nearly to redness; the remaining sulphate is readily soluble in boiling water, and yields, on evaporation, a gum-like mass, with no traces of crystallization; but if it be redissolved in sulphuric acid, the solution yields crystals which are still a neutral sulphate, and which may be freed from adhering acid by washing with alcohol; they contain water of crystallization. Ammonia throws down pure zirconia, free from sulphuric acid, from the solution of this sulphate: alcohol throws down a precipitate which, when well washed with alcohol, is a *tribasic sulphate* $= 3\text{ZrO},\text{SO}_3$. By saturating the concentrated solution of the neutral sulphate with hydrate of zirconia, an uncrystallizable *bibasic sulphate* may be obtained $= 2\text{ZrO},\text{SO}_3$. (BERZELIUS.) The neutral sulphate consists of

						Berzelius.
Zirconia	1	...	31	...	43·66 43·13
Sulphuric acid	1	...	40	...	56·34 56·87
<hr/>						
Sulphate of zirconia	1		71		100·00	100·00

AMMONIO-SULPHATE OF ZIRCONIA is precipitated on mixing a concentrated neutral solution of zirconia with sulphate of ammonia; it is soluble in water and in acids: its formation does not always succeed, and it is often immediately redissolved. (BERZELIUS.)

POTASSIO-SULPHATE OF ZIRCONIA. When a solution of a salt of zirconia is mixed with solution of sulphate of potassa, zirconia is precipitated: when sulphate of potassa is added, so as to saturate the liquor, the greater part of the zirconia falls, and the whole of it is thrown down on accurately neutralizing the acid of the liquor with potassa. This precipitate is partly soluble in pure water, and when washed the washings become turbid on dropping into the liquor which has run through; if the mixed liquor be boiled, a part of the precipitate dissolves in the free acid and falls again as it cools: but the undissolved portion has suffered a change which has not only rendered it insoluble in water, but also in sulphuric, nitric, and hydrochloric acids; it suffers a similar change by washing with boiling water. This insoluble compound is a basic salt, which contains six times the quantity of base contained in the neutral salt, combined with so small a quantity of potassa that one would regard

it as immaterial if the same precipitate were occasioned by sulphate of soda, which, however, is not the case. It is soluble in bicarbonate of ammonia, but again thrown down by boiling, retaining its insolubility in acids. This condition of insolubility shows that the zirconia has passed into that modification of the earth which is produced by sulphate of potassa, but not by sulphate of soda; to render it again soluble, it must be boiled or fused with caustic potassa and well washed, when pure hydrate will remain. When zirconia is fused with bisulphate of potassa, a double salt is formed, which is perfectly transparent whilst in its fused state: water dissolves bisulphate of potassa out of it, and leaves the difficultly soluble salt just noticed: when there is great excess of the acid salt, the fused product is wholly soluble in water. This property of zirconia of being thrown down by sulphate of potassa, is applicable to the freeing of the earth from iron and other foreign bodies. (BERZELIUS.)

PHOSPHATE, SELENITE, and CARBONATE OF ZIRCONIA are white insoluble salts: the carbonate falls in the state of hydrate, and is easily decomposed by heat.

CHARACTERS OF THE SALTS OF ZIRCONIA. These salts have an astringent taste; they are precipitated by caustic potassa, and the precipitate is not soluble in excess of the alkali. When boiled with sulphate of potassa a subsalt of zirconia subsides, the peculiarities of which, as stated by Berzelius, are above described. Infusion of galls produces in them a yellow precipitate, and phosphate of soda throws down a white phosphate of zirconia. The recently-precipitated carbonate of zirconia is soluble in excess of bicarbonate of ammonia, or of potassa. (See HERMANN, *on the Salts of Zirconia*. *Ch. Gaz.*, May, 1844.)

§ XL. YTTRIUM. Y. 32.

IN 1794 Professor Gadolin discovered a new earth in a mineral from the quarry of Ytterby, in Sweden, to which Ekeberg, in 1797, gave the name of *Yttria*. The mineral has since been termed *Gadolinite*. It is composed of yttria, silica, and the oxides of iron and cerium. Yttria has been found also to form about one-fifth of the weight of *yttrotantalite*, and about one-twelfth of that of *ytthrocerite*; and it occurs in the minerals termed *Orthite* and *Pyrorthite*, and in the *fluoride* and *phosphate of yttrium*. (See COLUMBIUM.)

The following is Vauquelin's process for obtaining yttria. (*Ann. de Ch.*, xxxvi. 150.) Fuse pulverized *Gadolinite* with twice its weight of potassa; wash the mass with boiling distilled water, and filter. The filtered solution, which has a beautiful green color, yields, during evaporation, a black precipitate of oxide of manganese. When this has ceased to appear, allow the liquor to stand; decant the clear part, and saturate with nitric acid. Let the insoluble part be also digested with extremely dilute nitric acid, which will take up the soluble earths only, and will leave undissolved the silica and oxide of iron. Let the two portions be mingled together, and evaporated to dryness; then redissolved and filtered; by which means any remains of silica and oxide of iron are sepa-

rated. To obtain the yttria from the nitric solution, it would be sufficient, if no other earth were present, to precipitate it by carbonate of ammonia; but small portions of lime, and of oxide of manganese, are still present along with it. The first is separated by a few drops of carbonate of potassa; and the manganese, by the cautious addition of hydrosulphuret of potassa. The yttria is then to be precipitated by pure ammonia, washed abundantly with water, and dried. It amounts to about 35, or, according to Berzelius, 45 *per cent.* of the weight of the stone.

Berzelius obtains yttria as follows: Gadolinite in fine powder is dissolved in nitrohydrochloric acid, and the solution decanted from the deposited silica: crystals of sulphate of potassa are then added to it, and it is left for 24 hours: in proportion as the fluid becomes saturated by the sulphate, a white or yellowish powder falls, which is a double sulphate of potassa and protoxide of cerium: this is separated, and the clear solution neutralized by caustic ammonia, and the oxide of iron thrown down by succinate of ammonia. The precipitate is separated by filtration, and the clear liquid precipitated by caustic ammonia, by which yttria (with a little oxide of manganese) is thrown down: the oxide of manganese may be separated by digesting this precipitate in a solution of carbonate of ammonia, filtering, and boiling, by which carbonate of yttria separates: this, being dried and heated to redness, leaves yttria.

Wöhler obtained *yttrium* in 1828 by acting upon *chloride of yttrium* by potassium, as in the process for the decomposition of zirconia; on washing the residue of this action, the yttrium remains in the form of grey metallic scales, brittle, and resisting the action of air and water: when heated in air or oxygen it burns brilliantly into yttria, which shows slight marks of fusion; it readily dissolves in dilute acids, and slowly in solution of potassa, but not in ammonia: it combines with sulphur, selenium, and phosphorus. (*Poggend.*, xiii. 580, and *Phil. Mag. and Ann.*, v. 393.)

It would appear from the experiments of Mosander that the substance hitherto supposed to be pure yttria is a mixture of that oxide with two others, to the bases of which he has given the names *Erbium* and *Terbium* (derived by alliteration from the word *Ytterby*). The whole of this investigation is at present so imperfect, that it is impossible accurately to define the separate characters of the three oxides, or to understand how far lanthanum or didymium (see *Cerium*, p. 904) may be connected with them, so that what follows must be considered as descriptive of the substance obtained under the name of yttria by the processes above mentioned. (*Phil. Mag.*, Oct. 1843. *Berzelius' Lehrbuch*, ii. 173.)

The atomic weight usually assigned to yttrium is 32: a number founded upon the analyses of certain of its compounds by Berzelius, and by Berlin. (*Poggend.*, xliii. 105.)

OXIDE OF YTTRIUM. YO. Yttria is insipid, white, and without action on vegetable colors. Its specific gravity = 4.842. It is insoluble in water, but very retentive of it; insoluble in pure alkalis, but soluble in carbonated alkalis. In carbonate of ammonia it is much less soluble than glucina. It forms salts which have a sweetish austere taste, and which have been little examined. They are decomposed by the pure alkalis, and by lime and baryta. Oxalic acid and oxalate of ammonia throw down a white bulky precipitate from the solutions of yttria, soluble in hydro-

chloric acid. Ferrocyanide of potassium occasions in them a white or grey granular precipitate of ferrocyanide of yttrium; phosphate of soda, a white gelatinous one; and tincture of galls throws down brown flocculi.

Yttria consists of

						Berzelius.
Yttrium.....	1	32	80 80.1
Oxygen	1	8	20 19.9
<hr/>						<hr/>
Yttria	1		40		100	100.0

CHLORIDE OF YTTRIUM is very soluble and deliquescent. When yttrium is heated in chlorine it burns brilliantly, and the resulting chloride sublimes in white acicular crystals. This chloride was obtained by Wöhler by passing dry chlorine over an intimate mixture of charcoal and yttria in a glass or porcelain tube heated to redness. The solution of yttria in hydrochloric acid is very difficultly crystallizable, and when evaporated to dryness the residue evolves hydrochloric acid and leaves yttria if heated to redness. (BERLIN. BERZELIUS.) Chloride of yttrium forms a double salt with chloride of potassium when the two are fused together; it evolves heat on solution in water. (BERZELIUS.)

IODIDE AND BROMIDE OF YTTRIUM. Yttrium burns when heated in the vapor of iodine or bromine; the resulting compounds are volatile, and form crystalline sublimates, fusible, and soluble in water with the evolution of heat. The solutions of yttria in hydriodic and hydrobromic acids are difficultly crystallizable. *Iodate of yttria* falls as a white precipitate soluble in 190 parts of water: when heated it explodes and evolves oxygen gas and the vapor of iodine. *Bromate of yttria* resembles the iodate, but is more soluble. (BERLIN.)

FLUORIDE OF YTTRIUM is an insoluble compound; it occurs *native*, combined with the fluorides of cerium and calcium, in the vicinity of Fahlun.

NITRATE OF YTTRIA is deliquescent, but by spontaneous evaporation it may be obtained in colorless crystals.

SULPHURET OF YTTRIUM. Yttrium burns in sulphur-vapor, and produces a pulverulent grey sulphuret, insoluble in water, but evolving sulphuretted hydrogen when acted on by acids. (WÖHLER.)

SULPHITE OF YTTRIA, YO,SO_2 , is formed by the direct action of aqueous sulphurous acid on hydrated yttria, or by precipitation with an alkaline sulphite: it is a white powder, insoluble in water, but sparingly soluble in solution of the acid, and when this solution is evaporated under exposure to air, it yields crystals of the sulphate. (BERLIN.)

SULPHATE OF YTTRIA, YO,SO_3 , is crystallizable and of a pale-pink hue; it is remarkable for its tardy solubility in water, and it is less soluble in dilute sulphuric acid, so that excess of acid facilitates its crystallization. It forms a double salt with sulphate of potassa, which is $= KO,SO_3 + YO,SO_3$: it is soluble in 16 of cold and 10 parts of boiling water. (BERLIN.)

SELENIURET OF YTTRIUM. Yttria combines with selenium with feeble ignition, when they are fused together; the compound is black, and does not decompose water; but on the addition of an acid, yields seleniuretted hydrogen. *Selenite of Yttria* falls in the form of white flakes when selenites of the alkalis are added to solutions of the salts of yttria; they dry into a white powder, insoluble in water and in excess of selenious acid. (BERZELIUS.)

PHOSPHURET OF YTTRIUM. Yttrium burns in the vapor of phosphorus, and produces a pulverulent grey phosphuret, which decomposes water with the evolution of phosphuretted hydrogen. (WÖHLER.)

PHOSPHATE OF YTTRIA. When a salt of yttria is mixed with a solution of common phosphate of soda, a white infusible powder falls, which is insoluble in water: when it is dissolved to saturation in nitric or in hydrochloric acid, the solution deposits a tribasic phosphate during evaporation. When it is dissolved in an acid, and precipitated by ammonia, a basic phosphate falls. A *native phosphate of yttria*, containing 62.6 yttria, 33.5 phosphoric acid, and 3.9 phosphate of iron, occurs near Lindesness, in Norway. (See Berzelius, in respect to some peculiarities of this salt.)

CARBONATE OF YTTRIA is found *native*: when thrown down by excess of carbonate of soda, and left in the liquor, it gradually forms small crystals: both are hydrated carbonates, which, when dried at 212° , lose one-third of their carbonic acid, and become anhydrous at about 285° ; at a red-heat the greater part of the carbonic acid is expelled, but it obstinately retains about 2 or 3 *per cent*. This carbonate is insoluble in water, and very sparingly soluble in aqueous carbonic acid: it gradually dissolves in solutions of ammoniacal salts, producing carbonate of ammonia. (GADOLIN. BERZELIUS. BERLIN.)

The components of the hydrated carbonate are

						Klaproth.	Berlin.
Yttria	1	...	40	...	44.94	55	} ... 69.76
Carbonic acid	1	...	22	...	24.72	18	
Water	3	...	27	...	30.34	27	
<hr/>							
Terhydrated carbonate of yttria	1		89		100.00	100	100.00

When this carbonate is digested in a solution of carbonate of ammonia, an *ammonio-carbonate of yttria*, in small crystals, is deposited: it is decomposed at a boiling temperature. (BERZELIUS.)

BORATE OF YTTRIA is obtained by double decomposition in the form of a bulky precipitate, which, during washing, absorbs carbonic acid and passes into a mixture of carbonate and acid borate of yttria. (BERZELIUS.)

CHARACTERS OF THE SALTS OF YTTRIA. They have a sweet astringent taste, not unlike those of glucina: their specific gravity exceeds that of the other earthy salts: some of them, when crystallized, have an amethystine tint, generally referred to the presence of manganese, but depending, according to Mosander, upon the presence of the foreign oxides already adverted to. They are thrown down of a white color by ferrocyanide of potassium, and by caustic potassa, and the precipitate is not soluble in excess of the precipitant. Carbonated alkalis, when added in excess, slowly redissolve the precipitate. The *sulphate* is the most characteristic salt.

§ XLI. THORINUM. Th. 60.

THIS substance was discovered by Berzelius in 1828, in a rare and complex mineral, found in the syenitic rock of the Isle of Loven, near Brevig, in Norway. It contained about 58 *per cent.* of *thorina* (*Poggend.*, xvi. 387,) which was obtained as follows: the mineral in powder was digested in hydrochloric acid, which formed a gelatinous mass, which, evaporated to dryness, and digested in dilute hydrochloric acid, left silica. The hydrochloric solution was then freed from lead and tin, by a current of sulphuretted hydrogen, and the clear solution saturated by ammonia: this occasioned a precipitate, which was washed, dissolved in dilute sulphuric acid, and the solution evaporated to a small bulk; during this evaporation *sulphate of thorina* was deposited, which, being washed with a saturated solution of sulphate of potassa, was dissolved in boiling water, and decomposed by caustic potassa, which threw down the thorina in the state of a white powder. (*Ann. de Ch. et Ph.*, xliii. 5.)

By passing a current of dry chlorine over a mixture of thorina and charcoal-powder, a crystalline *chloride of thorinum* is obtained, which is easily decomposed by potassium, and the product is *thorinum*. It is of a grey color, metallic lustre, and apparently malleable. It is not oxidized by hot or cold water, but when heated in the air it burns with great brilliancy into thorina, which is snow-white, and shows no traces of fusion. It is feebly acted on by sulphuric acid, and scarcely by nitric acid: it is not attacked by the caustic alkalis at a boiling heat. Hydrochloric acid dissolves it, with the evolution of hydrogen. Its apparent equivalent is 60. (59·6 GMELIN.)

OXIDE OF THORINUM. THORINA, ThO, obtained as above described, and after having been heated to redness, is white, and insoluble in the acids, with the exception of the sulphuric. When thrown down in the state of *hydrate*, it dissolves more readily, and exposed to the air absorbs carbonic acid. It probably consists of

						Berzelius.
Thorinum	1	...	60	...	88	88·17
Oxygen	1	...	8	...	12	11·83
<hr/>						<hr/>
Thorina	1		68		100	100·00

Thorinum combines energetically with chlorine, sulphur, and phosphorus. The *chloride* has been above adverted to: the other compounds have been but imperfectly examined.

Thorina is distinguished from the other oxides by the following properties: from alumina and glucina, by its insolubility in pure potassa; from yttria, by forming with sulphate of potassa a double salt, which is quite insoluble in a cold saturated solution of sulphate of potassa; from zirconia, by the circumstance that this earth, after being precipitated from a hot solution of sulphate of potassa, is almost insoluble in water and the acids. Thorina is precipitated also by ferrocyanide of potassium, which does not separate zirconia from its solutions. Berzelius has remarked that sulphate of thorina is much more soluble in cold than in hot water, so that a cold saturated solution becomes turbid when heated, and in cooling recovers its transparency. (TURNER'S *Elements*.)

§ XLII. ALUMINUM. Al. 14.

THE term *aluminum* or *aluminium* has been applied to the metallic base of the earth *alumina*, a substance of common occurrence in the mineral world, and of great importance in its applications to the arts. The nature of alumina was discovered by Davy in 1808, (*Elem. Chem. Phil.*, 355,) who found that potassa was generated by passing the vapor of potassium over white-hot alumina: he did not, however, determine the properties of its base. This has since been more accurately effected by Wöhler, to whom we owe the following ingenious method of obtaining it. (*Ann. Ch. et Ph.*, Jan. 1828, and *Poggend. Ann.*, xi. 146.) *Chloride of aluminum* is heated with clean and pure potassium (or sodium?) in a small platinum or porcelain crucible: the heat of a spirit-lamp is sufficient, for when the substances begin to act, the temperature suddenly rises to redness, and care should be taken so to adjust the relative proportions of materials, that none of the chloride may be evaporated in an undecomposed state, while at the same time there should not be excess of alkali in the residue. When the crucible is cold, its contents are well-washed with cold water, by which a finely-divided grey substance, with a certain degree of metallic lustre, is obtained, which is pure aluminum. To avoid the loss of materials which is apt to ensue in consequence of the violence of the action when the potassium and chloride act upon each other, Liebig introduces the chloride of aluminum into the sealed end of a small tube retort made of thin and difficultly fusible glass, and places the globules of potassium in the horizontal part of the tube; on heating the chloride, its vapor is decomposed by the potassium, the globules of which successively burn in it: when the operation is complete, the tube is broken, and the pieces thrown into water; when the aluminum has fallen, it is washed with alcohol, and dried.

Aluminum, as thus obtained, is in the form of a grey powder, much resembling platinum in appearance; it may be polished and flattened, by trituration in an agate mortar: it is extremely difficult of fusion; and although in the pulverulent state it does not apparently conduct electricity, it becomes a conductor when its particles are aggregated by heat. This, if not arising from imperfect contact, is an interesting fact, and holds good also, according to Wöhler, in the case of iron, which does not conduct when in very fine powder. Aluminum is not oxidized by exposure to dry air, but, when heated nearly to redness, it burns into a hard white substance, having the properties of alumina. When sprinkled into the flame of a spirit-lamp it scintillates like iron-filings, and if, when red-hot, it be immersed in oxygen, it burns with vivid light and intense heat: the result is fused alumina, apparently as hard as corundum.

Aluminum is not acted on by water at common temperatures, but when boiled it is slightly oxidized, and a little hydrogen is evolved: the oxidizement is, however, imperfect and superficial. It is not affected by nitric or sulphuric acids at common temperatures, but it rapidly dissolves in hot sulphuric acid, and sulphurous acid is evolved. The dilute acid dissolves it with the evolution of hydrogen, as is also the case with hydrochloric acid. It is soluble with the evolution of hydrogen in the caustic

fixed alkalis, and alkaline solutions of alumina are the results. It is similarly acted upon by ammonia, which in this case retains an unusual proportion of alumina in solution.

There is much difficulty in determining the equivalent of aluminum, arising out of the different views that may be taken of the atomic constitution of *alumina*, which is its only known oxide: some chemists regard it as a *protoxide*, and in that case a number intermediate between 9 and 10 would represent aluminum; others, from the analogy that subsists between some of the combinations of alumina and the peroxide of iron, have regarded it as a *sesquioxide*, namely as Al_2O_3 . Gmelin has adopted this view, and, with Turner and Graham, considers alumina as a *sesquioxide*, that is, as consisting of 2 atoms of aluminum and 3 of oxygen. Thomson represents alumina as a *protoxide*, and adopts 10 as the atomic weight of aluminum. Assuming alumina to be $= \text{Al}_2\text{O}_3$, I shall represent the atomic equivalent of aluminum by the number 14, which agrees well with the mean results of the best analyses of the aluminous compounds. (13.7 GMELIN. 13.72 GRAHAM.)

OXIDE OF ALUMINUM. SESQUIOXIDE OF ALUMINUM. ALUMINA. Al_2O_3 . 1. To obtain pure *alumina*, we decompose a solution of pure *alum* by excess of carbonate of potassa, wash the precipitate with repeated portions of hot distilled water, redissolve it in hydrochloric acid, precipitate it again by ammonia, thoroughly edulcorate, and dry the precipitate: it is rendered anhydrous by exposure to a red-heat. In this process, the alumina which first falls always retains a little potassa, which is got rid of by the second solution, and precipitation by ammonia: if ammonia be used as the original precipitant of a solution of alum, the resulting precipitate retains subsulphate of alumina, not decomposable by excess of ammonia. 2. Pure alumina may also be obtained, according to Gay Lussac (*Ann. Ch. et Ph.*, v. 102), by igniting pure *ammonia-alum*, previously deprived of water of crystallization by heat: sulphate of ammonia evaporates, and alumina remains, perfectly white, and very soft to the touch, but nevertheless, almost insoluble in acids. As thus obtained, its extreme division, and the hardness of its particles, observes Gay Lussac, might render it useful for polishing metal, and its whiteness for the preparation of colors. 3. Gregory obtains pure alumina as follows: a solution of alum is precipitated by excess of chloride of barium, sulphate of baryta is thrown down, and chlorides of aluminum, potassium, and barium remain in solution; on evaporation, hydrochlorate of alumina, along with chlorides of potassium and barium remain, and by igniting this residue the hydrochlorate is decomposed, and alumina, with the other chlorides, remains; the latter are removed by water.

Alumina is a colorless, insipid, and insoluble powder, without action upon vegetable blues: its specific gravity is 2; but after exposure to an intense heat, about 4. (ROYER and DUMAS.) By the oxyhydrogen blow-pipe it may be fused into a colorless globule. It has a strong attraction for moisture, which it rapidly absorbs from humid air to the amount of one-third its weight. When mixed with water, alumina is characterized by the plasticity of the mixture; and if the paste be dried in the air, and then heated, it shrinks considerably in consequence of the loss of water; this shrinkage was applied to Wedgwood to pyrometrical

purposes (p. 49). Alumina has a strong affinity for various organic compounds, and its use in the arts of dyeing and calico-printing depends upon its attraction for different coloring-principles, and for ligneous fibre. If ammonia be added to a solution of alum in infusion of cochineal, or of madder, the aluminous earth falls in combination with the red coloring-matter, and the supernatant liquor remains colorless. Colors thus prepared are called *Lakes*.

Moist alumina is readily soluble in most of the acids; but after the expulsion of its water by heat, it is much more difficultly dissolved, or even insoluble. It is sparingly soluble (when moist) in caustic ammonia; (see MALAGUTI and DUROCHER, *Ann. Ch. et Ph.*, Aug. 1846;) but potassa and soda readily dissolve it, and it is also soluble, to a certain extent, in the aqueous solutions of baryta and strontia. The fixed alkaline solutions of alumina are decomposed by the acids and by ammoniacal salts.

Alumina, like other sesquioxides, is a comparatively feeble base; none of its salts are, in fact, neutral, but have an acid reaction; and in respect to the more powerful basic oxides, it has been represented as performing the part of an acid, so that such compounds have been termed *Aluminates*. Many of these combinations exist native. Alumina is recognised by its solubility in caustic potassa; by the formation of octohedral crystals of alum on evaporating its sulphuric solution with the addition of sulphate of potassa, and the astringent sweetness of this salt; and by the fine blue color which it affords when moistened with nitrate of cobalt and strongly heated: this, according to Berzelius, is a very characteristic test.

Alumina, in reference to the above-mentioned equivalent, will consist of

						Berzelius.	Davy.
Aluminum....	2	...	28	...	53·8	53·3	56
Oxygen	3	...	24	...	46·2	46·7	44
Alumina.....	1		52		100·0	100·0	100

Native Alumina may be said to constitute the *sapphire*, which occurs either colorless or pale-blue, is extremely hard, and occasionally crystallized: its specific gravity is about 3·5. The oriental *ruby* and the oriental *topaz* are red and yellow varieties of sapphire. These gems are mostly found in alluvial deposits in Ceylon and Pegu: they have also been met with in France and Bohemia. *Corundum*, *adamantine spar*, and *emery*, are minerals also consisting chiefly of alumina, with less than 2 *per cent.* of oxide of iron, and a little silica: the sp. gr. of corundum is about 4. All these substances are extremely hard, being, in that respect, second only to diamond. By intensely heating hydrate of alumina moistened by a drop or two of solution of bichromate of potassa, in the flame of the oxyhydrogen blow-pipe, Gaudin succeeded in forming an artificial ruby. (*Ann. der Pharm.*, xxiii. 234.)

HYDRATES OF ALUMINA. When alumina is precipitated from its solutions in the state of hydrate, washed, and dried at between 70° and 80°, it always contains about 59° *per cent.* of water, although its physical characters vary considerably, dependant upon the strength of the solution from which it is precipitated: if from a saturated solution of alum, it forms a friable, opaque, spongy mass; if from a dilute solution, a

transparent, yellowish, gum-like, or gelatinous substance, which has no earthy characters, and does not adhere to the tongue. The composition of these hydrates, dried below 80° , is

Alumina	1	52	41.9
Water	8	72	58.1
<hr/>					
Octohydrate of alumina	1		124		100.0

Dried at 212° , this hydrate loses about 5 atoms of water, and becomes $\text{Al}_2\text{O}_3 + 3\text{HO}$. Exposed to a red heat, the *gelatinous* hydrate still loses only about 43 *per cent.* of its water, and the residue, under these circumstances, consists of

Alumina	1	52	74.3
Water	2	18	25.7
<hr/>					
Bihydrate of alumina	1		70		100.0

By protracted heat, further portions of water may be expelled, but the residue cannot be rendered anhydrous.

On the other hand, the *pulverulent* or *spongy hydrate*, loses the whole of its water at a red-heat, and hence, in analyses, it is always desirable that the alumina should be thrown down in the spongy and not in the gelatinous state, as in the latter case an error in the estimation of its quantity might ensue. The gelatinous alumina may, however, be brought to the state of the spongy, by moistening it with sulphuric acid and giving it a red-heat; both the water and the acid are then entirely driven off.

Native Hydrate of Alumina constitutes the mineral called *Gibbsite*, from Richmond in Massachusetts: it occurs in small stalactitic aggregates of a fibrous texture, and of a greenish-white color: its density is 2.4, and it contains about 35 *per cent.* of water. According to Mitscherlich, a corresponding hydrate may be artificially formed by digesting excess of recently-precipitated hydrate of alumina in a solution of caustic potassa, at a moderate temperature, and either preserving the filtered solution in a well-closed flask, or suffering it slowly to absorb carbonic acid from the air; in each case, small white translucent crystals are gradually formed, which contain about 35 *per cent.* of water, not expelled at 212° . *Gibbsite*, therefore, and these crystals, are composed of

Alumina	1	52	65.8
Water	3	27	34.2
<hr/>					
Terhydrate of alumina	1		79		100.0

The mineral called *Diaspore*, (from its property of decrepitating into powder when heated,) is a native *bihydrate of alumina* $= \text{Al}_2\text{O}_3 + 2\text{HO}$.

ALUMINATE OF POTASSA. KO, AlO_3 , is obtained by dissolving alumina precipitated by carbonate of ammonia in solution of potassa; or by fusing anhydrous alumina with excess of potassa. The solution evaporated in vacuo yields hard brilliant crystals of hydrated aluminate of potassa, very soluble in water, insoluble in alcohol, of a caustic taste, and alkaline reaction. A certain quantity of water decomposes this salt,

precipitating alumina, and retaining a highly alkaline aluminate. (Fremy, *Ann. Ch. et Ph.*, Nov., 1844.) The crystals contain

Potassa	1	...	48	...	37·8	...	Fremy. 37·5
Alumina.....	1	...	52	...	40·9	...	40·6
Water	3	...	27	...	21·3	...	21·2
<hr/>							
Crystallized aluminate of potassa	1		127		100·0		99·3

ALUMINATE OF SODA is more difficultly crystallized than the preceding. The other aluminates are insoluble, and formed by double decomposition.

CHLORIDE OF ALUMINUM. SESQUICHLORIDE OF ALUMINUM. Al_2Cl_3 . This compound has been mentioned as a source of *aluminum*: it was obtained by Wöhler, as follows:—Alumina, in the state of pulverulent hydrate, is mixed into a paste with powdered charcoal, oil, and sugar, and this is heated in a covered crucible till the organic matter is decomposed: an intimate mixture of the alumina with charcoal is thus obtained, which is introduced whilst hot into a proper porcelain or glass tube, placed in a convenient furnace: dried chlorine is then passed through it into a receiver attached to the other end of the tube, and the air being thus expelled, the tube is heated red-hot, and chlorine gradually passed into it: carbonic oxide is disengaged, and chloride of aluminum formed, which chiefly collects within the tube, and ultimately plugs it up. It is a crystalline translucent substance of the color of chlorine; it fumes and deliquesces when exposed to air; it is energetically acted upon by water, and is very soluble in alcohol: it may be preserved in naphtha. If a solution of alumina in hydrochloric acid be concentrated by spontaneous evaporation in a dry atmosphere, crystals are obtained containing 44·7 *per cent.*, or 12 equivalents of water. (BONSDORFF.) When the solution is evaporated by heat, a deliquescent hydrated chloride remains (hydrochlorate), which, at a higher temperature, evolves hydrochloric acid, and leaves alumina, so that chloride of aluminum cannot be thus obtained. The components of this chloride are

Aluminum	2	...	28	...	20·6
Chlorine	3	...	108	...	79·4
<hr/>					
Chloride of aluminum	1		136		100·0

Chloride of aluminum absorbs gaseous ammonia, at first slowly, and then so rapidly as to evolve much heat: the compound is partially decomposed by water: it is $= 3NH_3, Al_2Cl_3$. When heated in an atmosphere of ammoniacal gas, it loses a portion of its ammonia, and heated in an atmosphere of hydrogen it passes into NH_3, Al_2Cl_3 . (H. ROSE, *Poggend.*, xxiv. 298. PERSOZ, *Ann. Ch. et Ph.*, xlv. 320.) Chloride of aluminum also absorbs sulphuretted hydrogen when heated in a tube and exposed to a current of the gas: the combination sublimes in white pearly crystals, very deliquescent, and decomposed by solution in water. (WÖHLER.) Heated in a stream of phosphuretted hydrogen, a crystalline sublimate is obtained, which evolves phosphuretted hydrogen when dissolved in water, or in aqueous ammonia: it is $PH_3, 3Al_2Cl_3$. (H. ROSE. *Poggend.*, xxiv. 295.)

CHLORATE OF ALUMINA is a deliquescent salt obtained by mixing a solution of silicofluoride of aluminum with a boiling saturated solution of chlorate of potassa, filtering, and evaporating. (BERZELIUS.) The solution of alumina in perchloric acid yields an uncrystallizable deliquescent *perchlorate of alumina* on evaporation, which is soluble in alcohol. (SERULLAS, *Ann. Ch. et Ph.*, XLVI. 304.)

IODIDE OF ALUMINUM has not been obtained in the solid state, but probably exists in solution when gelatinous alumina is dissolved in hydriodic acid. *Iodate of alumina*, obtained by dissolving hydrated alumina in aqueous iodic acid, is very deliquescent and imperfectly crystallizable.

BROMIDE OF ALUMINUM was obtained by D'Arcet, by the action of bromine at a high temperature upon a mixture of alumina and charcoal; in its principal properties it resembles the chloride. The solution of alumina in hydrobromic acid yields deliquescent acicular crystals soluble in alcohol. (BERTHEMOT. *Ann. Ch. et Ph.*, XLIV. 394.)

BROMATE OF ALUMINA is a very deliquescent uncrystallizable salt. (RAMMELSBERG. *Poggend.*, LV. 63.)

FLUORIDE OF ALUMINUM. Hydrate of alumina readily dissolves in hydrofluoric acid, and, on evaporation, a gummy substance is obtained, which bears a red-heat without entire decomposition. Berzelius has described two *alumino-fluorides of potassium* obtained from mixed solutions of the two fluorides. They are gelatinous precipitates which become white and pulverulent when washed and dried: they are represented by the formulæ $3KF + Al_2F_3$, and $2KF + Al_2F_3$. *Alumino-fluoride of sodium* occurs native in *Kryolite* $= 3NaF, Al_2F_3$, a rare mineral hitherto found only in Greenland: it consists of

							Berzelius.
Sodium	3	...	72	...	33.64	...	32.93
Aluminum	2	...	28	...	13.09	...	13.00
Fluorine	6	...	114	...	53.27	...	54.07
<hr/>							
Kryolite	1		214		100.00		100.00

NITRATE OF ALUMINA, Al_2O_3, NO_5 , is very difficultly crystallizable, and generally obtained, on evaporating its solution, in the form of a semitransparent gum-like mass, very deliquescent, and soluble in alcohol: it may be obtained by very careful evaporation in soft foliated crystals. When decomposed by caustic ammonia, a pasty precipitate separates, which is a *basic nitrate*, not decomposed by excess of ammonia. (BERZELIUS.)

SULPHURET OF ALUMINUM, Al_2S_3 , is obtained by dropping sulphur upon incandescent aluminum, or by passing the vapor of sulphur over red-hot aluminum. A black compound is the result, which is decomposed by exposure to air, and which, when thrown into water, deposits alumina, and evolves sulphuretted hydrogen. (WÖHLER.) When an aluminous salt is decomposed by an alkaline hydrosulphuret, alumina is thrown down, and sulphuretted hydrogen is evolved.

HYPOSULPHITE OF ALUMINA. No precipitate falls when oxalate of alumina is added to hyposulphite of lime. (HERSCHEL.)

SULPHITE OF ALUMINA. When a solution of alumina in aqueous sulphurous acid is evaporated in vacuo, a gum-like mass remains, which gradually passes into a sulphate by exposure to air: when its solution is heated to about 165°, sulphurous acid is evolved, and a white pulverulent *hydrated basic sulphite* falls, which is insoluble in water, but soluble in aqueous sulphurous acid: this basic salt soon passes into sulphate when exposed to air: when boiled in water it is decomposed, sulphurous acid evolved, and hydrated alumina deposited: when heated to redness, it leaves alumina retaining a little sulphuric acid, the whole of which is expelled by longer exposure to a red heat, and pure alumina remains. (FOURCROY and VAUQUELIN. GOUGGINSBERG, *Ann. der Pharm.*, XLV. 132; BERTHIER, *Ann. Ch. et Ph.*, L. 371.) It consists of

						Gougginsperg.
Alumina	1	...	52	...	43·33 43·10
Sulphurous acid	1	...	32	...	26·67 27·04
Water	4	...	36	...	30·00 29·86
<hr/>						
Hydrated basic sulphite of alumina	1		120		100·00	100·00

HYPOSULPHATE OF ALUMINA was obtained by Heeren, by mixing solutions of hyposulphate of baryta and sulphate of alumina, filtering, and allowing the liquor spontaneously to evaporate, when very small crystals were deposited: on evaporating the filtered solution to dryness in vacuo, a white mass was obtained, the solution of which was copiously precipitated by chloride of barium, so that a pure hyposulphate of alumina cannot apparently be obtained. (*Poggendorff*, vii. 180.)

TERSULPHATE OF ALUMINA, $Al_2O_3,3SO_3$, is formed by digesting hydrate of alumina in sulphuric acid diluted with an equal bulk of water; the solution is evaporated and alcohol added, which throws down the tersulphate. It dissolves in 2 parts of water, and forms small lamellar crystals, of a sweet and astringent taste, which include 18 atoms of water. When excess of hydrated alumina is boiled in the diluted acid, and the solution filtered and evaporated in vacuo over sulphuric acid, it congeals into a soft, white, semitransparent mass, which may be dried on blotting paper, and is not altered by the air. According to Kane, as quoted by Gmelin, the most perfect tabular crystals are obtained from the solution of the salt in hydrochloric acid. Exposed to heat, this salt loses water of crystallization, and an *anhydrous sulphate* remains. By long exposure to a red-heat, the whole of the acid is expelled. The solution of this salt may be used as a test for potassa; for when it is dropped into a strong solution of that alkali or its salts, small crystalline grains of alum are thrown down. It consists, when anhydrous, of

Alumina	1	...	52	...	30·23
Sulphuric acid	3	...	120	...	69·77
<hr/>					
Anhydrous tersulphate of alumina	1		172		100·00

The crystallized salt contains

Alumina	1	...	52	...	15·57	} ... 51·50
Sulphuric acid.....	3	...	120	...	35·93	
Water	18	...	162	...	48·50	
<hr/>						
Crystallized tersulphate of alumina	1		334		100·00	100·00

This sulphate is found native in the volcanic island of Milo, in the Archipelago, and elsewhere. (MILL, *Quart. Journ. Sc.*, iii. 382; BOUSSINGAULT, *Ann. Ch. et Ph.*, xxx. 109, and Lii. 348.)

SULPHATE OF ALUMINA. BASIC SULPHATE OF ALUMINA. $\text{Al}_2\text{O}_3, \text{SO}_3, 9\text{HO}$. When ammonia is added to a solution of sulphate of alumina, a white powder falls, which is not decomposed by excess of ammonia, and which, when well washed and carefully dried, consists of

						Stromeyer.	
Alumina	1	...	52	...	30·05	...	29·87
Sulphuric acid	1	...	40	...	23·12	...	23·37
Water	9	...	81	...	46·83	...	46·76
<hr/>							
Hydrated basic sulphate of alumina	1		173		100·00		100·00

This compound, in the preceding state of hydration, exists *native*, forming the mineral called *Aluminite*, or *Websterite*: it occurs near New-haven on the coast of Sussex; at Halle in Germany; at Bernon near Epernay; and at Auteuil near Paris: its usual geological position is in the plastic clay immediately upon chalk.

BISULPHATE OF ALUMINA. $\text{Al}_2\text{O}_3, 2\text{SO}_3$. When the preceding basic sulphate is boiled in a solution of the tersulphate and filtered whilst hot, an uncrystallisable salt is obtained on gently evaporating the liquor, having, according to the analysis of Göbel and Maus, the above composition. Several other aluminous sulphates have been described; but there is no satisfactory evidence of their definite atomic constitution.

SULPHATE OF ALUMINA AND POTASSA. COMMON ALUM. POTASH ALUM. $\text{KO}, \text{SO}_3; \text{Al}_2\text{O}_3, 3\text{SO}_3; 24\text{HO}$. This useful salt is manufactured upon an extensive scale in Britain. *Aluminous slate*, which is an argillaceous slaty rock containing sulphuret of iron, is roasted so as to oxidize the iron and acidify the sulphur: on lixiviating the roasted ore, a *sulphate of alumina* is obtained, which, with the addition of *sulphate of potassa*, yields alum. The *shales* or wastes of old coal-mines, which fall down in a decaying or decomposing state, yield on lixiviation, especially after prolonged exposure to air and moisture, considerable quantities of sulphate of alumina and sulphate of iron: the solution of these salts is evaporated at the alum-works, near Glasgow, in large brick cisterns, by carrying the flue of a furnace over its surface, and, when sufficiently concentrated, is run out into coolers, where the sulphate of iron crystallizes, and the sulphate of alumina, being the much more soluble salt, remains in the mother-liquors: to these, when heated, sulphate or chloride of potassium is added, and they then yield crystals of alum, not at first pure, but rendered so, and obtained in beautifully-perfect octohedral crystals, by

recrystallization. The potassa salts required for this manufacture are often obtained by burning common sea-weed, collected upon the coast; the ash, or *kelp*, contains salts of potassium, which are purified by crystallization: the mother-liquors, which were formerly thrown away, are now resorted to as sources of *iodine* (p. 286). When chloride of potassium is used, it decomposes the sulphate of iron of the alum-liquors, forming chloride of iron and sulphate of potassa; the latter salt goes to the formation of alum, leaving the chloride of iron in solution.

There are many other methods of manufacturing alum, such as by the decomposition of clay by sulphuric acid, and by the lixiviation of certain *alum stones*, as they are called, which are products of the joint action of sulphurous acid and oxygen upon volcanic rocks containing alumina and potassa; these abound in the Solfaterra, near Naples, and yield what is termed *Roman alum*: it differs from common alum in crystallizing in opaque cubes, and appears to contain more alumina than common octohedral alum: when this variety is dissolved in cold water and slowly crystallized, it reappears in cubic crystals; but if dissolved in water heated to 110° , or higher, a subsulphate of alumina falls, and octohedral alum is obtained. Roman alum has not been accurately analyzed.

Octohedral alum has a sweet and astringent taste, accompanied by some degree of acidity; its sp. gr. is 1.72: it reddens vegetable blues: it dissolves in about 15 parts of cold water, and in about its own weight of boiling water (18.5 cold and 0.75 boiling water, GRAHAM). According to Poggiale, 100 parts of water dissolve 3.29 of alum at 32° , 9.52 at 50° , 22.01 at 86° , 30.92 at 122° , 90.67 at 158° , and 357.48 at 212° . The specific gravity of an aqueous solution of alum saturated at 46° is 1.045. The crystals are permanent in the air, or only very slightly efflorescent in a dry atmosphere; when heated, they fuse in their water of crystallization, at a temperature below 212° , and when this is expelled by the application of a sufficient heat, the dry alum becomes opaque and spongy, and in this state is generally termed *roche alum*, or when further dried, *burnt alum*. At a temperature of 140° , alum gradually loses 18 atoms of its water of crystallization. (GRAHAM.) When long retained in fusion at 212° , it loses 18.95 *per cent.* of water, and ultimately forms a vitreous mass, which retains 14 atoms of water: if in this state it be kept at a temperature of 248° , for 12 hours, the loss of water amounts to about 38 *per cent.*, and it forms a porous mass retaining 5 atoms of water; in this state it remains unchanged up to 320° ; but at 356° it sustains a farther loss of water amounting on the whole to 43.5 *per cent.*, so that the residue only retains one atom of water, the whole of which is not expelled under a temperature approaching to redness. (HERTWIG, *Poggend.*, LV. 99). Burnt alum gradually absorbs water from the atmosphere, acquiring about 18 atoms in 47 days. When freshly prepared anhydrous alum is put into water, it appears almost insoluble and remains for a long time nearly unchanged; but if previously exposed for fourteen days to the atmosphere it then dissolves much more readily. Alum is almost insoluble in an aqueous solution of tersulphate of alumina. (GMELIN.) At a red-heat alum first loses that portion of its acid belonging to the alumina, and ultimately the sulphate of potassa is itself decomposed under the influence of the alumina, which combines with the potassa and displaces the sulphuric acid. When pulverized alum is triturated with oil of vitriol it

evolves heat and forms a pasty mass which concretes on cooling: heated with chloride of potassium or sodium it evolves hydrochloric acid. When a saturated solution of alum is boiled with chloride of potassium, hydrochloric acid is formed and a difficultly soluble basic alum deposited: this change is more difficultly effected with chloride of sodium, and scarcely at all with chloride of ammonium. A solution of alum with nitre and common salt dissolves gold. The octohedral crystals of alum consist of

						Graham.
Sulphate of alumina	1	...	172	...	36.13	} ... 54.11
Sulphate of potassa	1	...	88	...	18.48	
Water	24	...	216	...	45.39	
<hr/>						<hr/>
Crystallized potash-alum	1		476		100.00	100.00

Or of

						Berzelius.	Thomson.
Alumina.....	1	...	52	...	10.92	10.76	11.09
Potassa	1	...	48	...	10.08	9.95	9.86
Sulphuric acid	4	...	160	...	33.68	33.74	32.85
Water	24	...	216	...	45.32	45.55	46.20
<hr/>						<hr/>	<hr/>
	1		476		100.00	100.00	100.00

CUBIC ALUM. If the quantity of carbonate of soda necessary to neutralize a portion of alum be divided into three equal portions, and added in a gradual manner to the aluminous solution, it will be found that the alumina first precipitated is redissolved upon stirring, and that no permanent precipitate is produced till nearly 2 parts of alkaline carbonate are added. It is in the condition of this partially-neutralized solution that alum is generally applied as a mordant to cloth. Animal charcoal readily withdraws the excess of alumina from this solution, and so does vegetable fibre, probably from a similar attraction of surface. When this solution is concentrated by evaporation, alum crystallizes from it, generally in the cubic form, and the excess of alumina is precipitated. (GRAHAM.) If hydrated alumina be boiled with a solution of alum an insoluble double salt is formed = $\text{KO}, \text{SO}_3; 3[\text{Al}_2 \text{O}_3, 3\text{SO}_3] + 9\text{HO}$. (RIFFAULT, *Ann. Ch. et Ph.*, xvi. 355.) A similarly constituted compound appears to exist *native* in the alumstone of Tolfa.

Alum is a salt of extensive use in the arts, more especially for the preparation of mordants employed by the dyer and calico-printer; it is also extensively employed in preparing and preserving skins; in pharmacy it is used as an astringent and a styptic, and burnt alum is a mild escharotic. It is necessary for many purposes that alum should be perfectly free from oxide of iron, the presence of which is ascertained by the addition of excess of caustic potassa, and heating the solution; the alumina is taken up, but the oxide of iron remains.

HOMBERG'S PYROPHORUS. When potassa-alum is ignited with charcoal, a spontaneously-inflammable compound results, which has long been known under the name of *Homberg's pyrophorus*. The potassa is decomposed in this process, along with the acid of the alum, and pyrophorus is probably a compound of sulphur, charcoal, and potassium, with alumina; or of charcoal, alumina, and sulphuret of potassium. Pyro-

phorus is most successfully prepared by the following process. Mix equal parts of honey, or of brown sugar, and powdered alum, in an iron ladle, melt the mixture over a fire, and keep it stirred till dry: reduce the dry mass to powder, and introduce it into a green glass phial coated with clay, and placed in a crucible of sand. Give the whole a red heat, and when a blue flame appears at the neck of the phial, allow it to burn about five minutes; then remove it from the fire, stop the phial, and allow it to cool, taking care that air cannot enter it. (See *Sulphate of Potassa*.)

SULPHATE OF ALUMINA AND AMMONIA. AMMONIA-ALUM. NH_4O , SO_3 ; $\text{Al}_2\text{O}_3, 3\text{SO}_3$; 24HO . This salt is obtained exactly as the preceding, only *sulphate of ammonia* is substituted for sulphate of potassa: its atomic constitution also resembles that of potash alum, and it is so similar in other respects, that, as far as mere appearance and more obvious properties are concerned, the two salts are not readily distinguished. It is recognised by evolving ammonia, when triturated with lime or potassa. This variety of alum was formerly much in use, and the requisite ammonia was chiefly derived from putrid urine: it is also largely prepared with the sulphate of ammonia derived from gas works. (See p. 399.) When heated it loses water, then ammonia, and at a very high heat, its acid, the residue being pure alumina. The solubility of this species of alum has not been accurately determined, but it probably is not widely different from that of potassa-alum: it occasionally occurs *native* in certain coal strata, as for instance, at Tschermig in Bohemia. Its components are

Ammonia	1	...	17	...	3·72	} Sulphate of ammonia } =Tersulphate of alumina } Water	1	...	57	...	12·55
Alumina	1	...	52	...	11·45		1	...	172	...	37·89
Sulphuric acid	4	...	160	...	35·27		25	...	225	...	49·56
Water.....	25	...	225	...	49·56						
<hr/>											
Crystals of ammonia-alum }	1		454		100·00		1		454		100·00

Maus (*Poggend.*, xi. 81), and Riffault (*Ann. Ch. et Ph.*, xvi. 359), have described two varieties of *basic ammonia-alum*.

SULPHATE OF ALUMINA AND SODA. SODA-ALUM. NaO, SO_3 ; $\text{Al}_2\text{O}_3, 3\text{SO}_3$; 24HO . This salt, which has also been found *native* (SHEPARD, *Silliman's Amer. Journ.*, xvi. 203), is formed when the sulphate of potassa of common alum is replaced by sulphate of soda; it crystallizes in octohedra, which are less hard, smooth, and regular, than those of potassa-alum; their sp. gr. is 1.6; they effloresce in dry air, and at 110° to 120° , become opaque and gradually lose their water of crystallisation, the whole of which is expelled at a red heat, and the residue is not perfectly soluble in water. (URE, *Quart. Journ.*, viii. 386.) They dissolve in 2.14 of water at 55° , and in their own weight at 212° : the hot saturated solution concretes, on cooling, into a mass of imperfect crystals: this salt is insoluble in absolute alcohol. It consists of

					Zellner.	Ure.	Graham.
Soda	1	32	6.95	6.67	6.48	}	52.53
Alumina	1	52	11.31	11.00	10.75		
Sulphuric acid	4	160	34.78	34.32	34.00		
Water	24	216	46.96	48.01	49.00		
Crystallized soda-alum	1	460	100.00	100.00	100.23		100.00

SULPHATE OF ALUMINA AND LITHIA. LITHIA-ALUM. $\text{LO}, \text{SO}_3; \text{Al}_2 \text{O}_3, 3\text{SO}_3; 24\text{HO}$. When an aqueous solution of sulphate of lithia and tersulphate of alumina is subjected to spontaneous evaporation at a temperature not exceeding 52° , it yields octohedral and rhombic dodecahedral crystals soluble in 24 parts of cold, and 0.87 of boiling water. (KRASLOVANSKY, *Schweigger's Journ.*, liv. 349): they consist of

Lithia	1	15	3.38
Alumina	1	52	11.76
Sulphuric acid.....	4	160	36.11
Water	24	216	48.75
Crystallized lithia-alum	1	443	100.00

						Kraslovansky.
Sulphate of lithia	1	55	12.41 13.56
Tersulphate of alumina	1	172	38.82 35.83
Water	24	216	48.77 50.61
<hr/>			<hr/>		<hr/>	<hr/>
	1		443		100.00	100.00

SULPHATE OF ALUMINA AND MAGNESIA. MAGNESIA-ALUM. $\text{MgO}, \text{SO}_3; \text{Al}_2 \text{O}_3, 3\text{SO}_3; 24\text{HO}$. This salt (containing, according to Gmelin, 25HO) is found *native*, constituting a species of *plumose alum*: it contains 2.17 per cent. of oxide of manganese: it has been analysed by Stromeyer. When a mixed solution of sulphate of magnesia and tersulphate of alumina with great excess of acid is subjected to spontaneous evaporation in a rough porcelain basin, it forms groups of acicular crystals $= 3[\text{MgO}, \text{SO}_3] + [\text{Al}_2 \text{O}_3, 3\text{SO}_3] + 36\text{HO}$. (KLAUER, *Ann. der Pharm.*, xiv. 264.)

SULPHATE OF ALUMINA AND MANGANESE. $\text{MnO}, \text{SO}_3; \text{Al}_2 \text{O}_3, 3\text{SO}_3; 24\text{HO}$ ($25\text{HO}?$) This salt occurs *native* in transparent silky fibres, much resembling common alum in taste and solubility, but not crystallisable in octohedrons. In this salt MnO, HO , appears to be equivalent to KO , or to $\text{NH}_4 \text{O}$, comparing it with potassa-alum, and ammonia-alum. (KANE. APJOHN, *Poggend.*, xlv. 471.)

SULPHATE OF ALUMINA AND IRON. The substance known under the name of *plumose alum*, which occasionally forms amianthine silky crystals or fibres upon decomposing pyritical clay-slate, is of variable composition, but appears essentially to consist of sulphate of alumina and sulphate of iron. A specimen analyzed by R. Phillips (*Ann. Phil.*, xxi. 446) may be represented by the formula $6[\text{FeO}, \text{SO}_3] + [\text{Al}_2 \text{O}_3, 2\text{SO}_3] + 48\text{HO}$. Another specimen, analysed by Berthier, and the so-called *mountain butter* (Bergbutter) described by Brandes (*Schweigger's Journ.*, xxxix. 417) may be represented by $2[\text{FeO}, \text{SO}_3] + [\text{Al}_2 \text{O}_3, 3\text{SO}_3] + 27\text{HO}$.

Another variety analyzed by Rammelsberg (*Poggend.*, xliii. 399), appears to be a true *iron-alum*, and similar to the salt obtained by Klauer, by exposing a mixed solution of protosulphate of iron and tersulphate of alumina, with great excess of acid, to spontaneous evaporation (*Ann. der Pharm.*, xix. 261): its formula is $\text{FeO},\text{SO}_3 + \text{Al}_2\text{O}_3,3\text{SO}_3 + 24\text{HO}$. Bouis (*Journ. de Chim. Med.*, xii. 628) has described a ferro-magnesian sulphate of alumina forming a concretionary efflorescence upon a decomposing pyritical schistus: it appears to be $\text{FeO},\text{SO}_3 + \text{MgO},\text{SO}_3 + \text{Al}_2\text{O}_3, \text{SO}_3 + 15\text{HO}$. (GMELIN, *Handbuch*, iii. 262.) When freshly precipitated hydrated alumina is agitated in an aqueous solution of persulphate of iron, it abstracts the whole of the oxide of iron and the greater part of the sulphuric acid, leaving a little alumina in solution: if there be excess of the salt of iron, it remains unaltered. The resulting compound after having been washed with hot water is readily soluble in cold dilute sulphuric acid, and difficultly so in dilute hydrochloric and nitric acid: a large proportion of its alumina is abstracted when it is digested in aqueous potassa. (ANTHON. *Buchner's Repertorium*.)

SELENIURET OF ALUMINUM. When selenium and aluminum are heated together to redness, they combine with ignition and form a black pulverulent compound which evolves hydroselenic acid when acted upon by water. (WÖHLER.) A solution of hydroseleniate of potassa produces a flesh-colored precipitate with salts of alumina, which gives off selenium at a red-heat. (BERZELIUS.)

SELENITE OF ALUMINA, $\text{Al}_2\text{O}_3,3\text{SeO}_2$, is insoluble, and produced when chloride of aluminum, deprived by evaporation of excess of acid, is dissolved in water and precipitated by selenite of ammonia. A solution of alum is not precipitated by selenious acid, a neutral alkaline selenite being requisite. The precipitate is a white powder, which, at a red-heat, first loses water and then acid. When either this selenite, or hydrated alumina, is dissolved in selenious acid and the solution evaporated, a gum-like colorless transparent salt remains which is $\text{Al}_2\text{O}_3,6\text{SeO}_2$. (BERZELIUS.)

SELENIATE OF ALUMINA, $\text{Al}_2\text{O}_3,3\text{SeO}_3$, resembles the corresponding sulphate, and forms similar basic salts. (BERZELIUS.)

PHOSPHURET OF ALUMINUM. Heated in the vapor of phosphorus aluminum enters into ignition and produces a grey powder, which is slowly acted upon by cold water, but evolves phosphuretted hydrogen in hot water. (WÖHLER.)

HYPOPHOSPHITE OF ALUMINA. A cold aqueous solution of hypophosphorous acid saturated with hydrated alumina, filtered, and evaporated in vacuo, leaves a viscid compound which, exposed to dry air, becomes a brittle gum-like substance, not deliquescent: heated in a retort, it evolves phosphuretted hydrogen, and a reddish substance remains. (H. ROSE, *Poggend.*, xii. 86.)

PHOSPHITE OF ALUMINA is thrown down on adding a solution of per-

chloride of phosphorus saturated with ammonia to a concentrated solution of alum: the precipitate at first redissolves, but afterwards becomes permanent, and is increased by boiling the fluid: it is a white powder, which heated to redness in a retort gives off hydrogen and vapor of phosphorus, and leaves a white residue. (H. ROSE, *Poggend.*, ix. 39.)

PHOSPHATES OF ALUMINA. Common phosphate of soda gives a gelatinous precipitate with solution of alum, which dries into a white insipid powder, insoluble in water and in solution of sal-ammoniac, but soluble in acids and in solution of potassa. When fused it yields a white enamel. It may be obtained in combination with different proportions of water, exclusive of which it appears to be $\text{Al}_2\text{O}_3, \text{PO}_5$. When its solution in an acid is precipitated by excess of caustic ammonia, a more basic compound falls, which appears to be $4[\text{Al}_2\text{O}_3] + 3\text{PO}_5 + 18\text{HO}$. A phosphate of alumina $= \text{Al}_2\text{O}_3, 3\text{PO}_5$, has not been as yet separately obtained. The mineral known under the name of *Wavellite* (having been originally discovered in the clay slate of Devonshire, by Dr. Wavell of Barnstaple) is a *hydrated phosphate of alumina*, being according to the analysis of Fuchs, $3\text{Al}_2\text{O}_3; 2\text{PO}_5, 12\text{HO}$. Fluoride of aluminum is considered by Berzelius as one of its essential constituents, but this seems doubtful, inasmuch as specimens have been found which contain no traces of fluorine. Berzelius represents it by the formula $3[4\text{Al}_2\text{O}_3, 3\text{PO}_5] + \text{Al}_2\text{F}_3 + 18\text{HO}$. According to the analysis of John (*Ann. des Mines*, 2 Ser. iii. 231), the *Turquoise* or *Calaité* is a phosphate of alumina $= 2\text{Al}_2\text{O}_3, \text{PO}_5 + 5\text{HO}$, colored by oxide of copper, and occasionally with traces of oxide of iron.

PHOSPHATE OF ALUMINA AND AMMONIA has been found *native* in the form of an earthy powder in a volcanic grotto in the Isle of Bourbon. (BERZELIUS.)

PHOSPHATE OF ALUMINA AND LITHIA is thrown down on adding a solution of a salt of alumina to phosphate of lithia. It has not been intelligibly analysed. Combined with fluoride of lithium it appears to exist in a rare mineral found near Chursdorff in Saxony, and termed *Amblygonite*. (BERZELIUS.)

PHOSPHATE OF ALUMINA AND MAGNESIA occurs as a hydrate in the mineral termed *Lazulite* from the neighbourhood of Werfen in Saltzburgh: it is $= 2\text{MgO}, \text{PO}_5 + 2\text{Al}_2\text{O}_3, \text{PO}_5 + 2\text{HO}$. (FUCHS. *Schweigger's Journ.*, xxiv. 373.)

CARBONATE OF ALUMINA. The precipitate which falls on the addition of a carbonated alkali to a solution of a salt of alumina is not carbonate of alumina, but alumina retaining a portion of the carbonate employed. Hydrate of alumina is sparingly soluble in water saturated with carbonic acid, but exposure to air destroys the combination, and pure hydrated alumina falls; so that no carbonate of alumina exists. (SAUSURE, *Jour. de Phys.*, lii. 28.)

CYANIDE OF ALUMINUM appears not to exist: hydrated alumina is

insoluble in hydrocyanic acid, and no compound has been obtained by double decomposition.

SULPHOCYANIDE OF ALUMINUM crystallizes in octohedra, which are persistent in the air. (GRAHAM.) According to Rammelsberg, this salt cannot exist except in solution, and its supposed crystals are those of alum.

BORATE OF ALUMINA may be formed by boiling recently-precipitated alumina with excess of boracic acid; it is uncrystallizable, and of a very astringent taste. At a red-heat it fuses into a glass. The neutral borate is insoluble.

ARSENIATE OF ALUMINA. This salt may be obtained by mixing solutions of alum and arseniate of soda; it is a white powder, insoluble in water but soluble in arsenic acid.

CHROMATE OF ALUMINA is formed by digesting hydrate of alumina in chromic acid, and neutralizing excess of the latter by ammonia; or by warming chromate of baryta in a solution of sulphate of alumina, or of alum, digesting the precipitate in dilute hydrochloric acid, and precipitating by ammonia. By digesting chromate of alumina in chromate of potassa, a *chrome-alum* is formed. (G. SPARKES.)

VANADIATE OF ALUMINA is a yellow powder, sparingly soluble in water.

Tellurate, molybdate, tungstate, columbate, and antimoniate of alumina are insoluble salts. (BERZELIUS.)

ALLOYS OF ALUMINUM. Aluminum probably exists in some of the varieties of cast-iron and steel. By fusing highly-carburetted steel with alumina, a peculiar alloy results, which is white, granular, and brittle, and which yields, on analysis, 6·4 *per cent.* alumina. On fusing 67 parts of this alloy with 500 of steel, a compound is obtained which possesses all the characters of the best Bombay *wootz*, and like it, when its surface is polished and washed over with dilute sulphuric acid, exhibits the striated appearance called *damask*, for which the celebrated sabres of Damascus are remarkable, and which renders it probable that they also are made of *wootz*. (*Quarterly Journal of Science and Arts*, ix.)

CHARACTERS OF THE SALTS OF ALUMINA. These salts have an astringent, sweet, and subacid taste, and redden litmus: they are precipitated by the caustic fixed alkalis, but the precipitate is redissolved when they are added in excess. The precipitate by ammonia is not soluble to any extent in excess of that alkali. The alkaline carbonates throw down hydrated alumina, with the escape of carbonic acid, and the precipitate is nearly insoluble in excess of the precipitants. Sulphate of potassa, with a little sulphuric acid, added to a strong solution of alumina, throws down a white crystalline powder, which is *alum*: phosphate of soda produces a white flocculent precipitate of phosphate of alumina. Succinate of ammonia and infusion of galls occasion precipitates in strong aluminous solutions. When aluminous substances are heated by the blow-pipe with nitrate of cobalt, they acquire a blue color, which is only distinctly seen after the mixture has cooled, and by daylight.

§ XLIII. SILICIUM. Si. 15.

FROM experiments upon the action of potassium upon *silica*, Sir H. Davy concluded that that earth consisted of a peculiar inflammable basis, combined with about its weight of oxygen, and he called the basis *Silicium*. This estimate of the composition of silica was deduced from the quantity of potassium required for its decomposition; the subject has since received further elucidation, and the correctness of the above statement has, to a great extent, been confirmed. (*Phil. Trans.*, 1808.)

In the year 1824 silicium was obtained in its pure state by Berzelius, and from its properties, presently to be described, he has placed it, perhaps correctly, among the simple non-metallic combustibles; indeed, it bears a strong resemblance to boron. Before, however, we remove it from the class of bodies with which it has usually been associated, it may be well to wait till its general characters have been more satisfactorily studied. From the ample account of this substance, given by Berzelius, the following details are chiefly extracted.

He recommends, as the best source of silicium, the *silico-fluoride of potassium*, which is prepared by passing silico-fluoric acid into a solution of potassa, evaporating to dryness, and heating the residue nearly but not quite to redness. The salt thus obtained is to be well mixed with eight or nine-tenths of its weight of potassium, and the mixture introduced into a green glass tube and heated: before it acquires a red-heat, its contents become ignited, in consequence of the chemical action that ensues, and a brown mass is obtained, consisting of fluoride of potassium, siliciuret of potassium, and a portion of the undecomposed salt: this is thrown into cold water, which occasions the evolution of hydrogen, resulting from the action of the siliciuret, the potassium of which is converted into potassa, and the silicium set free. When the effervescence is over, and the fluid has become clear, it is poured off from the residue, which is again washed, allowed to subside, and separated by decantation as before. These first washings must be performed with cold water, otherwise the alkali re-acts on the silicium, which, however, may afterwards be thoroughly edulcorated with boiling water. It remains in the form of a dark-brown powder, infusible, and a non-conductor of electricity. Its properties are remarkably different before and after the application of a red heat: *before it has been heated* it burns easily in the air; but the superficial formation of silica prevents its entire combustion: in oxygen it burns brilliantly, and however carefully prepared it always produces a little moisture. It is not acted upon either by sulphuric, nitric, or nitrohydrochloric acid, even when aided by heat; hydrofluoric acid readily dissolves it, evolving hydrogen; it is also dissolved when heated in a solution of caustic potassa. Silicium, *after it has been heated*, (obtained, for instance, by washing that which has been partially burned in the air with dilute hydrofluoric acid, to remove the superficial silica,) sinks in sulphuric acid, is incombustible before the blowpipe and in oxygen, and is not acted on by hydrofluoric acid, nor by caustic potassa; but it is easily dissolved in a mixture of hydrofluoric and nitric acids.

Silicium may be perfectly oxidized, and entirely converted into *silica* or *silicic acid*, by mixing it with dry carbonate of potassa, and heating to redness; it burns at the expense of the oxygen of the carbonic acid, and a *silicate of potassa* is obtained. Fused nitrate of potassa has no action upon it, but the addition of a little dry carbonate of potassa causes immediate deflagration: this paradoxical appearance depends upon the circumstance that the attraction of silicium for oxygen is influenced by the presence of the alkali, which has a high attraction for silica: just as the effect of zinc upon water is influenced by the presence of an acid having an attraction for the oxide of zinc about to be produced. Carbonic acid is so weak that it does not prevent the action of the alkali: and as silicium has a stronger attraction for oxygen than carbon, it is oxidized at the expense of the carbonic acid. Nitric acid, on the other hand, is a strong acid, which entirely prevents this action of the alkali in the saltpetre upon the silicium; and silicium, at the temperature at which saltpetre fuses, does not become oxidized; but if the heat be raised to whiteness, the silicium is then speedily oxidized by the decomposition of the nitric acid, and intense combustion ensues. Heated with the hydrated caustic alkalis, silicium burns in the oxygen of the water which they contain. (BERZELIUS.)

The equivalent of silicium has been variously estimated; according to Berzelius, silica is composed of 51.6 oxygen, and 48.4 silicium, and regarding it as a *protoxide*, this would give 7.5 as the equivalent of silicium, for $51.6 : 48.4 :: 8 : 7.5$. But Berzelius considers silica as a compound of 1 atom of base + 3 oxygen, hence 22.5 is his equivalent of silicium, and silica would be represented by SiO_3 , or $22.5 + 24 = 46.5$. Others regard silica as a protoxide, and as composed of equal weights of base and oxygen, and in this case the equivalent of silicium has been assumed as identical with that of oxygen, or 8, an estimate not inconsistent with many good analyses, and conveniently applicable to the silicious compounds. Kühn (*Stöchiometrie*, iii.), and Gaudin (*Ann. Ch. et Ph.*, lii. 125), have represented silica as containing one atom of base + 2 of oxygen, a view which has been adopted by L. Gmelin (*Handbuch*, ed. 1844, ii. 399), and which, as he observes, recommends itself by the simplicity of the formulæ which arise out of it, as applicable to the natural and artificial silicious compounds; upon these and other grounds, which will appear in the sequel, I have adopted this view of the composition of silica, and shall consider the equivalent of silicium as = 15, and silica as SiO_2 .

OXIDE OF SILICIUM. SILICA. SILICIC ACID. SiO_2 . This, which is the only known combination of silicium with oxygen, is a very abundant natural product; it exists pure in some varieties of *rock-crystal*, and nearly pure in *flint**. It may be obtained by heating colorless rock-

* The following are the principal minerals containing silica pure or nearly so.

i. *Rock-crystal*, or *Quartz*, which may be considered as pure silica. It crystallizes in the form of a six-sided prism, ended by six-sided pyramids; some varieties are perfectly transparent and colorless; others white and more or less opaque.

Its specific gravity is 2.6. It is so hard as to give sparks when struck with steel, and is nearly infusible. The primitive crystal, which is very rare, is an obtuse rhomboid, the angles of which are $94^\circ 24'$, and $85^\circ 36'$. The finest specimens are brought from Madagascar and the Alps. The perfectly transparent crystals found

crystal to redness, quenching it in water, and reducing it to a fine powder; in this state it is silica almost perfectly pure. Fuse 1 part of this powder with 3 of carbonate of potassa in a silver or platinum crucible. Dissolve the resulting mass in water, add slight excess of hydrochloric acid, and evaporate to dryness. Wash the dry mass in boiling distilled water upon a filter, and the white substance which remains is silica. This is the usual process; but the earth obtained by simply reducing the colorless rock-crystal to powder is generally very pure, though it may sometimes contain traces of oxide of iron and manganese, and of alumina. A very pure silica may also be obtained, by the fusion of fine white sand, or powdered rock-crystal, with carbonate of lime: the resulting compound of lime and silica may be decomposed by dilute hydrochloric acid, and the product, after having been duly washed, is silica in the form of a light powder. When gaseous fluoride of silicium (fluosilicic acid) is passed into water, the silica which is precipitated, after having been washed and dried, is also very pure, and in a state of extreme mechanical division.

Silica, in its ordinary state, is a harsh white insipid powder, insoluble in water and in most other solvents; it has no action upon vegetable colors, and is infusible except in the intense heat of the flame of a spirit-lamp, urged by the oxygen blow-pipe: it then melts with difficulty into a colorless globule, and admits of being drawn into filaments, like glass. Its specific gravity is 2.66. It has been stated by Jeffreys, that at a very

near Bristol and in Cornwall, are sometimes called *Bristol and Cornish diamonds*. The fine crystals are cut into ornaments, and sometimes used as a substitute for glass in spectacles; they are then termed *pebbles*, and do not so readily become scratched as glass.

Brown and yellow crystals of quartz are found in great beauty in the mountain of Cairn Gorm, in Scotland, and are much admired for seal-stones, &c.; they are sometimes improperly termed topazes.

Purple quartz or *amethyst*, is tinged with a little iron and manganese. *Rose-quartz* derives its color from manganese. *Prase* or *green quartz*, contains actinolite; and *chrysoprase* is tinged of a delicate apple-green by oxide of nickel. *Avanturine* is a beautiful variety of quartz, of a rich brown color, which, from a peculiarity of texture, appears filled with bright spangles: the finest specimens are from Spain: it is often imitated. Small crystals of quartz, tinged with iron, are found in Spain, and have been termed *hyacinths of Compostella*.

ii. *Flint, Chalcedony, Carnelian, Onyx, Sardonyx*, and *Bloodstone*, or *Heliotrope*, and the numerous varieties of *Agates*, are principally composed of quartz, with various tinging materials.

iii. *Opal* is among the most beautiful productions of the mineral world; it is a compound of about 90 silica and 10 water, and is distinguished by its very

brilliant play of colors. The finest specimens come exclusively from Hungary. There is a variety of opal called *hydrophane*, which is white and opaque till immersed in water; it then resembles the former. The proportion of water with which silica is combined in the different varieties of opal is liable to so much fluctuation, that they can scarcely be regarded as definite hydrates.

Common opal is usually of a dirty white, and does not exhibit the colors of the noble opal; it contains silica and water, with a little oxide of iron, and is not of unfrequent occurrence. The substance called *menilite* from Menil Montant, near Paris, is nearly allied to common opal. It is found in irregular masses in a bed of clay.

iv. *Pitchstone*, so called from its resinous appearance, contains 73 per cent. of silica. *Obsidian*, a volcanic product, contains 78 per cent. of silica, and much resembles glass in appearance, and the different kinds of *pumice* are nearly of similar composition.

v. The substance called *mineral flour* (*Bergmehl*) appears from Dr. Traill's analysis to consist chiefly of silica mixed with organic matter; such at least was the case with a specimen which he analysed from West Bothnia on the confines of Swedish Lapland. (*Edinb. Phil. Trans.*, xv. 145.) It contained, when dried, 22.00 organic matter, 71.13 silica, 5.31 alumina, 0.15 oxide of iron (loss 1.41).

high temperature steam carries off silica in the state of vapor, thus establishing an analogy between silica and boracic acid.

When recently precipitated, and in the state of *hydrate*, silica is to a certain extent soluble in water and in the acids. The aqueous solution is tasteless, and, when evaporated, deposits gelatinous silica, which, on being dried, becomes again quite insoluble. The acid solutions exhibit no indication of saline combination, but when evaporated leave pure silica. Silica is often found in spring and mineral waters; and in some of the boiling or hot springs of Iceland it is contained in such quantities as to be deposited by them in the form of a porous incrustation. In combination with bases silica performs the part of an acid, which, though under ordinary circumstances extremely feeble, exhibits high affinities at elevated temperatures, and at a red-heat not only the carbonates, but many of the sulphates are decomposed by it. According to the view of the atomic constitution of silica above suggested, it will consist of

						Berzelius.	H. Rose.	Stromeyer.
Silicium	1	15	48.39 48.3 49.72 46
Oxygen	2	16	51.61 51.7 50.28 54
<hr/>								
Silica	1		31		100.00	100.0	100.00	100

CHLORIDE OF SILICIUM. SiCl_2 . Silicium burns, when heated in chlorine, or when a current of chlorine is passed over red-hot silicium in a porcelain tube, and a fuming liquid is the result, of a yellow color, extremely volatile and irritating to the nose and eyes, and which, exposed to moist air, forms hydrochloric acid and silica. Dropped into water it first floats upon that fluid, and is then dissolved, depositing gelatinous silica: hydrochloric acid is also formed. When potassium is heated in its vapor, it burns with the production of siliciuret and chloride of potassium. (BERZELIUS.) Chloride of silicium may also be obtained by passing dry chlorine over an intimate mixture of silica and finely-divided charcoal in a red-hot porcelain tube: the chloride may be condensed in a properly-cooled receiver; as it generally contains excess of chlorine it may be agitated with a little dry mercury and redistilled. (OERSTED. DUMAS. *Ann. Ch. et Ph.*, xxxiii. 267.) It does not congeal at 0° : it boils at about 122° . (SERULLAS.) Its components are

						Berzelius.
Silicium	1	15	17.24 17.3
Chlorine	2	72	82.76 82.7
<hr/>						
Chloride of silicium	1		87		100.00	100.0

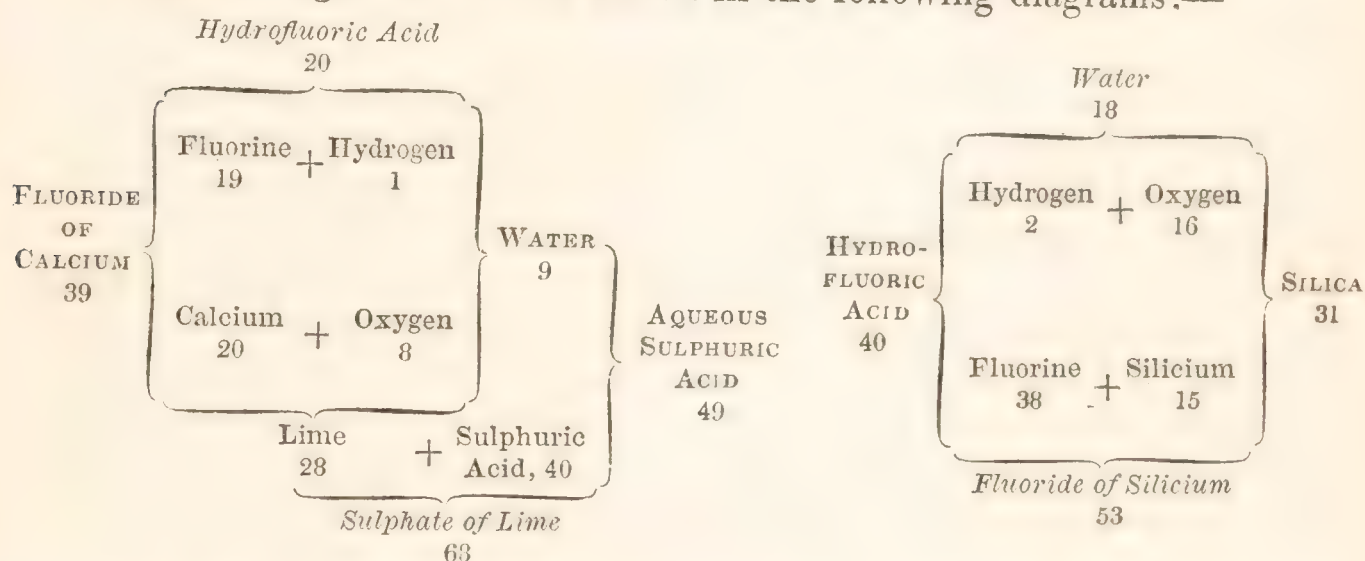
IODIDE OF SILICIUM has not been formed.

BROMIDE OF SILICIUM, SiBr_2 , is obtained by passing the vapor of bromine over heated silicium: it is a colorless fuming liquid, heavier than sulphuric acid. It congeals at 10° and boils at 300° . It is decomposed when gently heated with potassium, with explosive violence: water converts it into hydrobromic acid and silica. It may also be obtained by passing bromine vapor gradually through a red-hot porcelain tube, containing fragments of a compound formed by heating to redness in a covered crucible a pasty mixture of silica, lampblack, sugar, and oil, in such proportions that the charcoal is at least equal in weight to half that of the silica: a tubulated receiver surrounded by ice should be annexed

to condense the vapor, and the carbonic oxide produced during the operation should be allowed to escape through a long tube drawn out into a small opening, and inserted into the tubulure. The product obtained is bromide of silicium mixed with bromine; the latter may be abstracted by agitation in a retort with mercury, and the former distilled off. (SERULLAS, *Ann. Ch. et Ph.*, viii. 1; *Phil. Mag. and Ann.*, xi. 395.)

FLUORIDE OF SILICIUM. FLUOSILICIC ACID. SILICATED FLUORIC ACID. SiF_2 . The only acid body which acts energetically upon silica is the hydrofluoric acid: the result of this action is a gaseous compound. To obtain it, 4 parts of pulverized fluor spar and 3 of powdered glass, or 2 of silica finely powdered, are well mixed in a retort with about 5 parts of oil of vitriol; the gas evolved is to be collected over mercury, and when its production slackens, it may be accelerated by a gentle heat. The mercury and the glass vessels employed must be quite dry, for if in the least damp, they acquire an immovable film of silica. This decomposition depends upon the evolution of hydrofluoric acid and its action upon the silica, water and fluoride of silicium being the ultimate results. $\text{SiO}_2 + 2\text{HF} = \text{SiF}_2 + 2\text{HO}$. The hydrofluoric acid is derived from the action of the aqueous sulphuric acid on the fluoride of calcium; $\text{CaF} + \text{SO}_3, \text{HO} = \text{HF} + \text{CaO}, \text{SO}_3$.

These changes are further shown in the following diagrams:—



Fluoride of silicium is a colorless gas; its odor is acrid, somewhat resembling that of hydrochloric acid; its taste very sour; its specific gravity is 3.6 compared with air: 100 cubic inches weigh nearly 112 grains. It extinguishes the flame of a taper. It produces white fumes when in contact with damp air, and when exposed to water it is absorbed, and a soluble compound of silica with hydrofluoric acid is formed, whilst a quantity of silica is at the same time precipitated. According to Berzelius, one-third of the silica of the gas is deposited in the state of gelatinous hydrate, and the compound retained in solution consists of 2 atoms of silica and 3 of hydrofluoric acid; the action, therefore, of 3 atoms of fluoride of silicium upon 6 of water may be represented thus. $3\text{SiF}_2 + 6\text{HO} = \text{SiO}_2 + 2[\text{SiO}_2, 3\text{HF}]$. If the beak of the retort from which the gas is issuing be plunged into a basin of water, it is soon choked by the copious deposit of hydrated silica, which sometimes forms tubes through the water, by which the gas escapes directly into the air. When it is intended to saturate water with the gas (it takes up about 260 volumes), this effect may be prevented by agitation, or better by suffering the gas to

escape through a stratum of mercury into water above it. Water thus saturated becomes a gelatinous mass, from which the acid liquor may be separated, by placing it, without pressure, upon a linen filter. When this acid liquor is saturated with the fixed alkalis, it becomes gelatinous, but not turbid: with barytic salts it soon deposits a white precipitate.

Fluoride of silicium consists of

						J. Davy.	Berzelius.
Silicium	1	...	15	...	28·3	...	28·32
Fluorine	2	...	38	...	71·7	...	71·68
<hr/>							
Fluoride of silicium....	1		53		100·0		100·00

HYDROFLUOSILICIC ACID is one of the results of the above described action of fluoride of silicium on water. It may also be formed by saturating hydrofluoric acid diluted with 2 or 3 parts of water, with silica: if the acid be not sufficiently diluted, fluoride of silicium is evolved. Different views may be taken of the nature of the compound thus formed and held in aqueous solution. Gmelin states these as follows:—

(1)		(2)		(3)	
HF.....	20	SiO ₂	31	HO,HF.....	29
SiF ₂	53	3HF	60	SiO ₂ ,2HF	71
<hr/>		<hr/>		<hr/>	
73		91		100	

According to (1) the hydrofluosilic acid represents a metallic silicofluoride, in which the atom of metal is replaced by an atom of hydrogen; according to (2) it is a terhydrofluatate of silica; and according to (3,) it is a hydrated silicofluoride, if it be assumed that with water it would yield a hydrofluosilicate of a metallic oxide; for example, $\text{KF, SiF}_2 + 3\text{HO} = \text{KO, HF} + \text{SiO}_2, 2\text{HF}$. In this case, to form the hydrofluosilicic acid, the metallic oxide KO is replaced by HO. But it must be recollected that the hydrofluosilicic acid cannot be so far deprived of water as above represented; in its most concentrated state it contains, according to Berzelius, 3 atoms more of water than in (3), being, namely, $\text{HO, HF} + \text{SiO}_2, 2\text{HF} + 3\text{HO}$.

SILICOFLUORIDE OF AMMONIA. $\text{NH}_3, \text{SiF}_2$. 1 volume of gaseous fluoride of silicium condenses 2 volumes of ammonia, forming a white volatile pulverulent compound: in water it deposits silica, and yields hydrofluosilicate of ammonia. (J. DAVY.)

SILICOFLUORIDE OF HYDROFLUATE OF AMMONIA, $\text{NH}_3, \text{HF} + \text{SiF}_2$, is obtained in the form of a white sublimate by heating an intimate mixture of sal-ammoniac with silicofluoride of potassium or of sodium: it is also produced by neutralizing hydrofluosilicic acid with dilute ammonia: it forms hydrated prisms of a saline taste and reddening litmus.

SILICOFLUORIDE OF POTASSIUM, KF, SiF_2 , is formed by passing silicated fluoric acid into a solution of potassa; it falls in the form of an iridescent jelly, which dries into a white powder, very sparingly soluble in boiling water, and yielding minute anhydrous crystals. It appears that in the formation of this salt the potassa acting on the hydrofluoric acid forms fluoride of potassium, which combines with the fluoride of silicium.

This silicofluoride consists of

Potassium	1	...	40	...	5·71
Silicium	1	...	15	...	13·39
Fluorine	3	...	57	...	50·90
<hr/>					
Silicofluoride of potassium	1		112		100·00

SILICOFLUORIDE OF SODIUM, NaF, SiF_2 , is obtained in the same way as the potassium salt, but falls more readily, and is not iridescent: it is more soluble, especially in hot water. It may be obtained in small shining crystals, which are anhydrous hexangular prisms. It consists of

Sodium.....	1	...	24	...	25·00
Silicium	1	...	15	...	15·62
Fluorine	3	...	57	...	59·38
<hr/>					
Silicofluoride of sodium	1		96		100·00

SILICOFLUORIDE OF LITHIUM, LF, SiF_2 , forms microscopic six-sided prisms, scarcely soluble in pure water, but soluble in dilute acids. (BERZELIUS.)

SILICOFLUORIDE OF CALCIUM, CaF, SiF_2 , is formed by digesting carbonate of lime in aqueous hydrofluosilicic acid; also by digesting powdered fluor spar and silica in dilute hydrofluoric acid: on evaporation four-sided prisms are obtained, containing between 16 and 17 *per cent.* of water, and being therefore $\text{CaF}, \text{SiF}_2, 2\text{HO}$. (BERZELIUS.)

SILICOFLUORIDE OF BARIUM, BaF, SiF_2 , is gradually precipitated when silicofluoric acid is mixed with chloride of barium, in anhydrous microscopic crystals, of difficult solubility in water.

The *silicofluorides of strontium, magnesium, and lead*, are formed by dissolving their carbonates in silicofluoric acid. The salts of magnesium and of lead are very soluble. The *silicofluorides of manganese, iron, zinc, cobalt, nickel, and copper*, are soluble in water, and crystallize in similar hexagonal prisms, probably isomorphous.

SULPHURET OF SILICIUM. SiS_2 . Silicium, when heated intensely, burns brilliantly in the vapor of sulphur, and a white earthy compound is the result, which is not affected by dry air, and when heated to redness is slowly decomposed, with the production of sulphurous acid. It is rapidly decomposed by water; in moist air it exhales sulphuretted hydrogen, and that gas is abundantly evolved by its action on water, whilst the silica is retained in aqueous solution, and no sulphur is deposited. Sulphuret of silicium is composed, according to Berzelius, of 30 silicium and 70 sulphur, *per cent.*

PHOSPHURET OF SILICIUM has not been formed: when silicium is heated in the vapor of phosphorus no combination ensues. (BERZELIUS.)

CARBURET OF SILICIUM. When the potassium employed in the reduction of silica contains carbon, the resulting silicium is partly in the state of *carburet*; it has a dark color, and gives off carbonic acid when burned.

ALLOYS OF SILICIUM. Berzelius remarks that silicium only combines with the metals when in its nascent state, and that when once insulated no such compounds can be formed. When silica is reduced in contact of platinum, it becomes penetrated by silicium; but silicium may afterwards be heated white-hot in a platinum crucible without any such effect.

SILICATES. It is obvious from the preceding statement, that there are no salts, properly so termed, in which the oxy-acids are combined with silica, but that silicium forms haloid compounds. But silica readily combines, in the manner of an oxide or acid, with many of the salifiable bases; hence the term *silicic acid* applied to it, and *silicates* to its compounds. Of these compounds several are most importantly useful, and many of them are found as natural products, forming crystallized minerals, and parts of the strata or rocks that constitute the exterior crust of the globe. (See FOURNET, *Sur la Crystallization des Silicates Vitreux, &c.*, *Ann. Ch. et Ph.*, 3 Ser. iv. 370.) Glass, pottery, and porcelain, in all their varieties, are combinations of silica, and it is an essential ingredient in soils. I shall first describe some of the best defined silicates, and then briefly advert to the manufacture of glass, and of the different kinds of porcelain and pottery.

SILICATES OF POTASSA. When silica is fused with excess of carbonate of potassa, the oxygen in the carbonic acid expelled is equal to that of the silica; thus 1 atom of silica = SiO_2 expels 1 of carbonic acid = CO_2 . (H. ROSE.) 31 parts of silica fused with 70 carbonate of potassa, produce therefore the *neutral silicate of potassa*, composed of

Potassa	1	48	60·76
Silica	1	31	39·24
<hr/>					
Neutral silicate of potassa.....	1		79		100·00

When 1 part of silica and 4 of caustic potassa are fused together, and slowly cooled, a part of the compound may be poured out of the crucible before the whole has solidified, and pearly crystals of a silicate of potassa are formed in the residuary portion. (BERZELIUS.) These silicates are soluble in water, forming the *liquor silicum* of the older chemists. A similar solution may be obtained by digesting gelatinous hydrate of silica, or very finely-divided silica, in solution of potassa. The silica is thrown down from these solutions in the gelatinous state, by the acids. If an insufficiency of acid be added, the precipitate retains potassa; an excess of acid throws down the gelatinous hydrate, but a portion of silica remains in the solution, which is greater in proportion to the excess of acid and its state of dilution. (DALTON.) In very dilute solutions a considerable proportion of silica may thus be permanently retained. The salts of ammonia also precipitate the solution of silicate of potassa, inasmuch as their acid combines with the potassa, while ammonia is set free. Baryta, strontia, and lime water, and a solution of alumina in potassa, produce, when added to a solution of silicate of potassa, precipitates of double silicates (of potassa and the other base), while the excess of potassa is found free in the liquor. (GUYTON MORVEAU, *Ann. de Chim.*, xxxi. 246.)

BISILICATE OF POTASSA. $\text{KO},2\text{SiO}_2$. When about half its bulk of alcohol is added to a solution of gelatinous silica in excess of hot solution of potassa, the bisilicate separates underneath the alcoholic stratum, which is to be poured off, and the heavier portion diluted with water and again mixed with alcohol, and set aside for 24 hours: the lower layer separated and dried, is a bisilicate, (FORCHAMMER. *Poggend.*, xxxv. 339,) composed of

Potassa	1	...	48	...	43.64	Forchammer.	44.77
Silica	2	...	62	...	56.36	...	55.23
<hr/>							
Bisilicate of potassa	1		110		100.00		100.00

QUATERSILICATE OF POTASSA, $\text{KO},4\text{SiO}_2$, is obtained by fusing a mixture of 15 parts of pulverized quartz, and 10 of carbonate of potassa, into a perfect glass, reducing it to powder, and boiling it till dissolved, (for about 4 hours,) in 5 times its weight of water. (FUCHS. *Schweigger's Journ.*, xxiv. 378.) When aqueous solution of potassa is saturated with freshly precipitated hydrated silica this compound is also formed, and on evaporating the solution and fusing the residue, it remains in the form of a hard transparent glass. (FORCHAMMER.) It is composed of

Potassa	1	...	48	...	27.91	Forchammer.	28.43
Silica	4	...	124	...	72.09	...	71.57
<hr/>							
Quatersilicate of potassa	1		172		100.00		100.00

A concentrated aqueous solution of this compound, has the specific gravity 1.25; it is syrupy and viscid, and does not absorb carbonic acid from the atmosphere, which it does when dilute; it becomes covered by a tough film when exposed to air, and when applied as a varnish to wood and other materials, it dries upon them, and greatly diminishes their inflammability. It has thus been used for the scenery of theatres, applied as a ground, mixed with chalk or other body-color, to the wood or canvas, previous to its being painted upon. When a solution of this silicate is mixed with alcohol, and the precipitate washed with dilute alcohol till it no longer abstracts alkali, the residue is *octosilicate* = $\text{KO},8\text{SiO}_2$; and when this is boiled in water, the residue is $\text{KO},18\text{SiO}_2$. (FORCHAMMER.)

SILICATES OF SODA. The compounds of silica and soda are analogous to the preceding, but as carbonate of soda is not deliquescent, some of the soluble vitreous compounds which it forms effloresce on exposure, instead of running into a liquid, or remaining moist upon the surface. A solution of silica in soda has been employed as an addition to soap; it is said to improve its detergent powers. Silicates of soda always have a greenish or bluish tint, however pure the materials used in their production, and this is an obstacle to the substitution of soda for potassa in certain kinds of glass.

A neutral *silicate of soda*, NaO,SiO_2 , is formed by the fusion of a mixture of 31 parts of silica with 54 of anhydrous carbonate of soda. When silica is dissolved in solution of caustic soda in such proportion as to contain an atom of silica and an atom of soda, the concentrated solution concretes in a few days into crystals, some of which include 6,

and some 9 atoms of water; the former are oblique rhombic prisms, the latter rectangular prisms. (FRITZSCHE. *Poggend.*, xliii. 135.)

Tersilicate of Soda, $\text{NaO}, 3\text{SiO}_2$, is obtained by fusing together 100 parts of pulverized silica, and 40 of caustic soda: on rapidly cooling the resulting glass it is transparent, but if slowly cooled, it exhibits crystalline points; it is brownish, and contains about 24 *per cent.* of soda. (DUMAS.) When 3 parts of powdered quartz and 2 of dry carbonate of soda are fused together in a platinum crucible, the glass which results, after having been washed with cold water, yields a solution in boiling water from which alcohol throws down a white precipitate; when this is redissolved in water, and again precipitated by alcohol, it forms a transparent substance on drying, which is a *tersilicate*: this is said to be the compound held in solution in the waters of the geysers, or boiling fountains of Iceland. (FORCHAMMER. *Poggend.*, xxxv. 343.)

A *hydrated Quatersilicate of Soda*, $\text{NaO}, 4\text{SiO}, 12\text{HO}$, was obtained by Walcker (*Quart. Journ. Science and Arts*, 2nd Ser., iii. 371,) by saturating a boiling solution of caustic soda with precipitated silica, filtering, evaporating, and drying the residue at 242° : it is a pale yellow transparent glass, deliquescent, and difficultly soluble in water: when heated to redness it loses water, and becomes a spongy and very difficultly fusible mass which does not attract aërial moisture.

SILICATE OF LIME. Silica and lime may be combined by fusion, but the results of their mutual action have not been minutely examined. Under the article GLASS, in AIKIN'S *Dictionary*, some valuable facts will be found in reference to these combinations. There are some minerals which are silicates of lime. *Table spar*, or *Wollastonite*, is CaO, SiO_2 . (H. ROSE.) *Dauburite* is $\text{CaO}, \text{SiO}_2, \text{HO}$; (SHEPARD, *Silliman's Amer. Journ.*, xxv. 137;) and *Okenite*, or *Dysklasite*, is $\text{CaO}, 2\text{SiO}_2, 2\text{HO}$. (KOBELL.) *Apophyllite* is a *hydrated silicate of lime and potassa*, the formula of which is $\text{KO}, 8\text{CaO}, 15\text{SiO}_2, 16\text{HO}$. (STROMEYER.)

SILICATE OF BARYTA. 2 parts of silica and 1 of baryta fuse together into a porous slag. A similar combination may be obtained with *strontia*. (KIRWAN. VAUQUELIN.)

SILICATE OF MAGNESIA. Several minerals appear to be definite compounds of silica and magnesia. *Olivin*, and *chrysolite*, are disilicates of magnesia $= 2\text{MgO}, \text{SiO}_2$, with variable proportions of oxide of iron. *Villarsite*, a mineral analyzed by Dufrenoy, (*Comptes Rendus*, xiv. 698,) is $2[2\text{MgO}, \text{SiO}_2] + \text{HO}$; and the varieties of *noble serpentine* are *hydrated subsilicates of magnesia*. In the slags of smelting furnaces crystallized products are not unfrequent, which are *double silicates of lime and magnesia*. (BERTHIER; MITSCHERLICH, *Ann. Ch. et Ph.*, xxiv. 355.) Equal weights of lime, magnesia, and silica, may be fused into a green glass, which strikes fire with steel. (ACHARD.) 1 atom of lime, 1 of magnesia, and 2 of silica yield a pale bluish-green glass with granular fracture. Sefström and Berthier have described several of these double silicates, and a great variety of minerals are similarly constituted.

SILICATES OF MANGANESE. By fusing together 1 atom of silica and 2 of protoxide of manganese, Berthier obtained a crystalline silicate resem-

bling chrysolite. Thomson (*Mineralogy*, i. 514,) has described a mineral from New Jersey which is apparently $2\text{MnO}, \text{SiO}_2$, and there are several other native silicates and hydrated silicates of the oxides of manganese.

SILICATES OF IRON. These compounds are often found in the slags from the smelting of the ferro-sulphurets of copper. Davy found the ochraceous sediment of the chalybeate springs of Lucca to consist of *silicate of peroxide of iron*, the water probably holding a protosilicate in solution. There are several minerals which are silicates, or hydrated silicates of iron.

SILICATE OF ZINC occurs native under the name of *electric calamine*: it crystallizes in rhombic prisms, composed of 2 atoms of oxide of zinc, 1 of silica, and 1 of water.

SILICATE OF COPPER is thrown down of a green color upon the mixture of sulphate or nitrate of copper with silicate of potassa. It occurs native in *diopase*, or *copper-emerald*, which is $= \text{CuO}, \text{SiO}_2, \text{HO}$. The silicate of the *dioxide* of copper is of a deep purple, but it is difficult to obtain this tint of a pale color in glass, in consequence of the intense hue given by a small proportion of the oxide, and the facility with which, in a dilute state, it passes into green from the absorption of oxygen. Many of the ancient stained glasses, which were supposed to be colored by gold (or by purple of Cassius), derive their tints from copper, and are stated by Dumas to consist of a thin film of deep purple, attached to colorless glass: the ingenious process by which this was effected, consists in dipping the blowing-tube first into the deeply colored copper glass, and then taking up upon it a sufficient quantity of ordinary glass; on blowing, this extends so as to produce a thin transparent film of the copper glass upon the interior of the blown mass. A purple glass is obtained by fusing common glass with peroxide of iron and excess of sulphuret of copper, by which sulphuret of iron and dioxide of copper are formed: in this case, however, a little oxide of iron always remains in the glass. An opaque red or veined glass, is easily obtained by dioxide of copper.

SILICATE OF LEAD. This compound exists in flint-glass, and is often used as a glaze for porcelain or earthenware, hence the poisonous quality conferred upon certain articles of food, when kept in earthen vessels thus glazed. A silicate of lead is easily formed (of variable composition) by fusing silica with oxide of lead; a yellow glass is the result. Some of the Chinese figures (often said to be made of rice) are a glass composed of 41 oxide of lead, 39 silica, 7 alumina. (KLAPROTH.) The action of oxide of lead upon crucibles at a red-heat, arises out of the formation of this silicate.

SILICATE OF BISMUTH appears to exist native in the mineral termed *Bismuth Blende*, or *Bismuthite*, which, according to Kersten, (*Poggend.*, xxvii.,) contains $\text{BiO}_3, 2\text{SiO}_2$.

SILICATES OF ALUMINA. The different kinds of *clay* are probably mixtures, rather than compounds, of silica, alumina, and water. The best clays for the purposes of pottery are said to contain about 72 *per cent.* of silica and 28 of alumina. The following are the prin-

cipal varieties used here. 1. *Porcelain Clay*, derived principally from the decomposition of felspar, and containing silica and alumina, sometimes with traces of oxide of iron; it is very difficult of fusion. 2. *Marly Clay*, which, with silica and alumina, contains a portion of carbonate of lime; it is much used in making pale bricks, and as a manure; and when highly heated enters into fusion. 3. *Pipe Clay*, which is very plastic and tenacious, and requires a higher temperature than the preceding for fusion; when burned it is of a cream-color, and used for tobacco-pipes and white pottery. 4. *Potters' Clay* is of a reddish or grey color, and becomes red when heated; it fuses at a bright red-heat: mixed with sand it is manufactured into red bricks, and tiles, and is also used for coarse pottery*.

POTTERY AND PORCELAIN. The better kind of *pottery*, called in this country *Staffordshire ware*, is made of an artificial mixture of alumina and silica; the former obtained in the form of a fine clay, from Devonshire chiefly†, and the latter, consisting of chert or flint, which is heated red-hot, quenched in water, and then reduced to powder. Each material, carefully powdered and sifted, is diffused through water, mixed by measure, and brought to a due consistency by evaporation: it is then highly plastic, and formed upon the potter's wheel and lathe into various circular vessels, or moulded into other forms, which, after having been dried in a warm room, are inclosed in baked clay cases resembling bandboxes, and called *seggars*; these are ranged in the kiln so as nearly to fill it, leaving only space enough for the fuel; here the ware is kept red-hot for a considerable time, and thus brought to the state of *biscuit*. This is afterwards *glazed*, which is done "by dipping the biscuit-ware into a tub containing a mixture of about 60 parts of litharge, 10 of clay, and 20 of ground flint, diffused in water to a creamy consistence, and when taken out, enough adheres to the piece to give an uniform glazing when again heated. The pieces are then again packed up in the seggars, with small bits of pottery interposed between each, and fired in a kiln as before. The glazing-mixture fuses at a very moderate heat, and gives an uniform glossy coating, which finishes the process when it is intended for common white ware." (AIKIN'S *Dictionary*. Art. POTTERY.)

The presence of lead in glazes is often objectionable, and may be dispensed with by using borax, which, however, is too expensive for common use. A glaze, composed of 100 parts of silica, 80 pearlash, 10 nitre,

* It was my intention to have introduced in this place a summary of the composition of the principal minerals which come under the designation of *silicates*, and which, of course, are very numerous and important; but on referring to the best analytical authorities upon the subject, I have found insuperable difficulties in the way of perspicuously abridging their details or throwing the results of their inquiries into clear and useful formulæ; these difficulties arise partly out of the inherent complexity of the subject and the discrepancies of analysis, and partly out of the confused and eminently objectionable system of no-

menclature which prevails among mineralogists, the same mineral having frequently several names, and different minerals the same name; these names being indiscriminately derived from persons, places, properties, and things; so that notwithstanding the assistance which I might have derived from Rammelsberg, (*Wörterbuch des Chemischen Theils der Mineralogie*.) and from L. Gmelin, (*Handbuch*, II. 227.) I have been obliged to abandon the attempt.

† Fownes has detected traces of phosphoric acid in the clay which results from the decomposition of the felspar of the Dartmoor granite. (*Phil. Trans.*, 1844, 53.)

and 20 lime, fused into a glass and finely powdered, is said to be effectual. (*Chem. Gaz.*, October, 1843.) A variety of *glazed* cast-iron vessels for culinary and other purposes are now manufactured, in which the absence of lead in the glaze is most important: those made by Messrs. Clark, of Wolverhampton, receive two coats of glaze; the first, or under coat, is made by fusing together 66 parts of powdered calcined flint, and 34 of borax: 40 parts of this fused mass, and 5 of potters' clay, are then ground together in water, and applied in the liquid state to the clean surface of the iron: when this is dry enough to adhere, the outer coat is applied upon it in the form of powder, and the two coats fired together in a muffle: the outer glaze consists of 15 parts of borax, 73 of powdered plate, crown, or other glass free from lead, and 12 parts of soda.

The patterns upon ordinary porcelain, which are chiefly in blue, in consequence of the facility of applying cobalt, are generally first printed off upon paper, which is applied to the plate or other article while in the state of biscuit; the color adheres permanently to the surface when heat is properly applied.

The manufacture of *porcelain* is a most refined branch of art; the materials are selected with the greatest caution, it being necessary that the compound should remain perfectly white after exposure to heat: it is also required that it should endure a very high temperature without fusing, and at the same time acquire a semivitreous texture and a peculiar degree of translucency and toughness. These qualities are united in some of the Oriental porcelain, or *China*, and in some of the old Dresden, but they are rarely found co-existent in that of modern European manufacture. Some of the French and English porcelain, especially that made at Sèvres and at Worcester, is extremely white, and duly translucent, but it is more apt to crack by sudden changes of temperature; more brittle, and consequently requires to be formed into thicker and heavier vessels; and more fusible than the finest porcelains of Japan and China.

The colors employed in painting porcelain are the same metallic oxides used for coloring glass, and in all the more delicate patterns they are laid on with a camel-hair pencil, and generally previously mixed with a little oil of spike-lavender or of turpentine. Where several colors are used, they often require various temperatures for their perfection; in which case those that bear the highest heat are first applied, and subsequently those which are brought out at lower temperatures. This art of painting on porcelain or in enamel is of the most delicate description; much experience and skill are required in it, and with every care there are frequent failures; hence it is attended with considerable expense. The gilding of porcelain is generally performed by applying finely-divided gold mixed up with gum-water and borax; upon the application of heat the gum burns off, and the borax vitrifying upon the surface causes the gold firmly to adhere; it is afterwards burnished*.

CRUCIBLES. In the manufacture of various kinds of pottery employed in the chemical laboratory, and especially in regard to *crucibles*, many difficulties occur; and many requisites are necessary, which cannot be united in the same vessel: to the late Mr. Wedgwood we are indebted

* Porcelain, for *chemical purposes*, is now supplied of superior excellence from the Berlin and Dresden manufactories.

for vast improvements in this as well as in other branches of the art. Crucibles composed of one part of pure clay mixed with about three parts of coarse and pure sand, slowly dried and annealed, resist a very high temperature without fusion, and generally retain metallic substances; but where the metals are suffered to oxidize, there are few which do not act upon any earthen vessel, and some cause its rapid fusion, as the oxides of lead, bismuth, &c. Where saline fluxes are used, the best crucibles will always suffer, but platinum may often be employed in these cases, and the chemist is thus enabled to combat many difficulties which were nearly insurmountable before that metal was thus applied. Whenever silicious and aluminous earths are blended, as in the mixture of clay and sand, the compound softens, and the vessel loses its shape when exposed to a long-continued white heat, and this is the case with the *Hessian* crucibles: the most refractory of all vessels are those made entirely of clay, coarsely-powdered burned clay being used as a substitute for the sand. Such a compound resists the action of saline fluxes longer than any other, and is therefore used for the pots in glass-furnaces. A *Hessian* crucible lined with purer clay is rendered much more retentive; and a thin china cup, or other dense porcelain, resists the action of saline matters in fusion for a considerable time. Plumbago is a very good material for crucibles, and applicable to many purposes; when mixed with clay it forms a very difficultly-fusible compound, and is protected from the action of the air at high temperatures; it is well calculated for small table-furnaces. Wrought-iron, and the best cast-iron crucibles, are used for the fusion of several metallic substances which melt at a bright red-heat. The latter are used in the Mint for the fusion of silver; the gold is melted in black-lead or plumbago pots.

LUTES. Under the term *Lutes* a variety of compounds are used by the practical chemist for the purpose of securing the junctures of vessels or protecting them from the action of heat. Slips of wetted bladder, linseed meal made into a paste with gum-water, white of egg and quicklime, glazier's putty, which consists of chalk and linseed oil, and *fat lute*, composed of pipe-clay and drying oil, well beaten to a stiff mass, are very useful lutes for retaining fumes and vapors and joining vessels to each other, but earthy compounds are required to withstand the action of a high temperature. Windsor loam, or an artificial mixture of clay and sand well beaten into a stiff paste, and then thinned with water and applied by a brush in successive layers, to retorts, tubes, gun-barrels, &c., enables them to bear a very high temperature; if a thick coating is required, great care should be taken that the cracks are filled up as it dries, and often a little tow mixed up with the lute renders it more permanent and applicable. If the lute is intended to vitrify, as, for instance, to prevent the porosity of earthenware at high temperatures, a portion of borax or of red-lead may be mixed up with it. Respecting the selection and management of crucibles, lutes, &c., the reader is referred to Mr. Faraday's *Manipulation*.

MORTARS AND CEMENTS. *Mortar*, or the cement used in building, is a compound of several earthy substances, one of which is always lime; for much valuable information relating to this important subject we are indebted to the late Mr. Smeaton, (*History of the Eddystone Lighthouse*.)

and an excellent summary of the principal facts connected with it will be found in AIKIN'S *Dictionary*. (Art. CEMENTS.) The ordinary mode of making mortar consists in mixing a quantity of common sand with slaked lime, without any careful attention to the quantity or purity of the materials; but it has been shown by Smeaton, that the presence of unburnt clay prevents the induration of the mortar, and the sand used in London always contains it; the lime too is often imperfectly burned and seldom duly selected; that which contains a portion of alumina and oxide of iron being preferable to the purer varieties: hence the advantage of *Dorking lime* or *meagre lime*, as it is usually called. The sand should be sharp and large-grained, and perfectly free from salt, which always prevents the mixture from becoming hard. The addition of calcined ferruginous clay, or calcined basalt, or black oxide of iron, gives mortar the property of becoming hard under water.

The mutual action which the substances constituting the different kinds of mortar undergo, has hitherto been but imperfectly examined by the chemist; to M. Vicat we are indebted for a curious and important series of experiments upon this subject, and his work may be consulted with much advantage, by those who are concerned in investigations of this nature. (*Recherches Expérimentales sur les Chaux de Construction, les Bétons, et les Mortiers ordinaires*. Paris, 1818. See also *Ann. Ch. et Ph.*, 3 Ser. ii. 426; and in reference to all these subjects, DUMAS, *Chim. app. aux Arts*.)

MANUFACTURE OF GLASS. Of this important and extensive subject I have only room for a very brief outline: for details I must refer to the authorities quoted, to the volume of LARDNER'S *Cyclopædia*, which treats upon the manufacture of glass and pottery, and to DUMAS' work above quoted, and to URE'S *Dictionary of Arts, &c.*

GLASS is essentially composed of silica with potassa or soda, other substances being added for particular purposes. The silica used in the manufacture of glass, is of various degrees of purity; fine white sand is generally employed in this country; flints, and white quartz pebbles are also occasionally used. The alkali is either potassa or soda; purified soda or pearlash being preferred for fine glass; while less pure alkalis, such as wood-ash, barilla, and kelp, are used for common glass, where the impurities contained in those substances are of no importance. The alkali, originally in the state of carbonate, loses carbonic acid during combination with the silica; the quantity employed being usually about half the weight of the silica*.

* All common glass when reduced to a fine powder is more or less acted on by boiling water, which separates the alkali, and its entire disintegration seems only to be prevented by the insolubility of the silica. Indeed, if finely-powdered flint-glass be placed upon turmeric-paper and merely moistened, it powerfully reddens the test. Glass which has long been exposed to the weather frequently exhibits a beautiful iridescent appearance, and is so far decayed that it may be scratched with the nail: several years ago I examined some bottles of

wine which had lain in a wet cellar near the Bank, upwards of 150 years, having been deposited there (as circumstances proved) previous to the great fire of London in 1666. The glass was soft and greatly corroded upon the surface, in consequence of the abstraction of its alkali. The wine appeared to have been Malaga and Claret: the latter had perished, but the former was still vinous. See *Quart. Journ.*, xx. 262, where there is a paper on the solubility of glass by Mr. T. Griffiths.

A glass composed solely of silica and alkali requires a very high temperature for its perfect fusion, and is very difficult to work, so that various substances are added, with the intention of forming a more fusible, colorless, dense, and transparent compound: *oxide of lead*, in the form of litharge or minium, is very efficacious in this respect: it increases the fusibility of the compound, gives it greater tenaciousness when red-hot, increases its refractive power, and enables it to bear sudden changes of temperature. It is a copious ingredient in the *London flint-glass*, celebrated for its brilliancy when cut, and used for most optical purposes. But lead, though it confers these advantages, is productive of some evil; it renders the glass so soft as easily to scratch, and so fusible that it softens at a dull red-heat, a quality which, though sometimes desirable, is often disadvantageous in its chemical applications. It is also very difficult to obtain a mass of glass containing lead, of equal density throughout; it is generally wavy, a defect especially felt in selecting glass for optical purposes.

Boracic acid and borax form an admirable flux for glass-making, but the expense of those materials confines them almost entirely to the manufacture of artificial gems, or of glass applicable to particular purposes only.

Black oxide of manganese has long been used in glass-making; it was formerly called *glass-soap*, a term implying its power of cleansing certain impurities, and especially the green tinge which is apt to arise from impure alkali; but if it be added at all in excess, it communicates a purple tinge, more or less intense according to its quantity. This purple hue is destroyed by charcoal, or by thrusting a billet of wood into the glass-pot, which causes a slight effervescence, and the color disappears. There can be little doubt that the carbon acts by deoxidizing the manganese, for if a little nitre be added, the purple color returns. Lime in very small quantities, (8 or 10 parts of chalk to 100 of silica,) is sometimes added to glass: it acts as a flux, but it endangers the transparency of the compound.

White arsenic is also used as a very cheap and powerful flux; and nitre, in small quantities, is employed to destroy any impurities arising from carbonaceous matter.

The materials for the manufacture of glass are sometimes submitted to an operation called *fritting*, before they are transferred to the regular glass-furnace. It consists in exposing them to a dull red-heat, by which moisture and carbonic acid are expelled, and a slight degree of chemical action induced; this also prevents the excessive swelling up of the materials in the glass-pots, and renders the process of vitrification more certain and expeditious. The term *frit*, however, is now generally applied to the mere mixture of materials, which, without previous preparation, are at once melted in the furnace.

The glass-pots are placed round a dome-shaped furnace, built upon arches, and open beneath for the free admission of air; there are generally six in each furnace, and they are entirely enclosed except at an orifice on the side, opening into a small recess formed by the alternate projections of the masonry and the flues, in which recess the workmen stand. Coal is the fuel employed, and the furnace is so built that a rapid current of flame may be directed round each glass-pot, which afterwards passes out

with the smoke into the dome and chimney, heating a broad covered shelf in its passage, which is sometimes used as an annealing-oven.

In the construction of the furnace and pots, the greatest care is required; especially in the latter, which have not only to resist long-continued heat, but also, as far as possible, the action of ingredients which tend to accelerate their fusion or vitrification. They are usually made entirely of a refractory clay, one portion being crude or unburnt, and another calcined and powdered; the latter being the remains of former furnaces when pulled down for repairs.

The frit is introduced into the glass-pots through the side opening above-mentioned, and being heated to bright redness, becomes of a pasty consistency, and at length perfectly fuses. A quantity of impurities subside to the bottom of the pot, and partly rise to its surface. The scum known under the name of *sandever**, consists chiefly of saline substances, partly volatile at the high temperature of the furnace, which are removed from time to time, and sold to metal refiners as a powerful flux. The sandever, or *glass-gall*, being separated, the materials gradually become clearer, abundance of air-bubbles are extricated, and at length the glass appears uniform and complete; the fire round the individual pot is then damped till its contents acquire a consistency fit for working, the whole process requiring about 48 hours from the time the pots are filled. At the working-heat, which is a full red, the glass has a very peculiar tenacious consistency, and as it adheres but feebly to polished metal, it is easily wrought and managed with iron tools.

All glass articles require to be carefully *annealed*, that is, suffered to cool very slowly, otherwise they are remarkably brittle and apt to crack, and even fly into many pieces upon the slightest touch of any hard substance, as is well shown in the small drops of green glass suddenly cooled by dropping them into water, and called *Rupert's drops*; the instant their thin end is broken off, they crumble into a powder with a kind of explosion. This phenomenon, according to Mr. Aikin, "depends upon some permanent and strong inequality of pressure, for when they are heated so red as to be soft, and merely let cool of themselves, the property of bursting is lost, and the specific gravity of the drop increased." What are termed *Proofs*, or *Bologna phials*, are also made of unannealed glass, and fly to pieces when a piece of flint or other hard and angular substance is dropped into them.

When large masses of glass which have been long in fusion are suffered to cool slowly, they frequently exhibit very singular crystalline appearances; there are often detached globular formations, of a very peculiar radiated texture, and looking exactly like foreign substances imbedded in the glass; sometimes it is opaque and crystalline, bearing a strong resemblance to certain mineral products; in these cases crystallization seems to have influenced the affinity of the elements, and the consequent composition of the products. Mr. Watt's experiments upon the fusion of basalt may be consulted in reference to this curious subject. (*Phil. Trans.*) The specific heat of glass, as determined by Regnault, is

* This substance is scarcely known in our present glass-houses, in consequence of the pains bestowed upon the purification of the materials employed.

0.19768; but the composition of the specimen which he used is not stated. (*Ann. Ch. et Ph.*, Lxxiii. 34.)

The exact composition of the different kinds of glass is scarcely known; the following proportions of the materials are, however, given in Messrs. AIKINS' *Dictionary*, to which the reader is referred for a valuable article upon the subject of glass: it must, however, be recollected, that the composition of the perfect glass can only be remotely anticipated from a knowledge of the substances employed in its formation, in consequence of the changes which they undergo, and the volatility of some of them, at the high temperature to which they are subjected.

The materials employed in the manufacture of the different kinds of glass in common use, are stated to be as follows:

Flint-glass: Specific gravity about 3.2; 120 parts of fine clear white sand, 40 purified pearlash, 35 litharge, 13 nitre, a small quantity of black oxide of manganese.

Crown-glass, or best window-glass: 200 parts of soda, 300 fine sand, 33 lime, 250 ground fragments of glass*.

Green Bottle-glass: 100 parts of sand, 30 coarse kelp, 160 lixiviated earth of wood ashes, 30 fresh wood ash, 80 brick clay, 100 fragments of glass.

Plate-glass, invented by Abraham Thevart in 1688, was first manufactured in Paris. It may be composed of 300 lbs. fine sand, 200 lbs. soda, 30 lbs. lime, 32 oz. manganese, 3 oz. cobalt azure, 300 lbs. fragments of good glass. These materials are brought into perfect fusion, and poured upon a hot iron or copper-plate; the mass is then rolled out, annealed, and afterwards polished by grinding with sand, emery, and colcothar. The difficulty of producing a perfect plate without specks, bubbles, or waves, may easily be conceived, and this, with the risk of breakage, renders a large plate extremely expensive. The influence of long-continued exposure to light upon the color of plate glass, and its tendency under such circumstances to acquire a pink or purple tint, is referable to the presence of excess of oxide of manganese. (See p. 171.)

Mr. Faraday has communicated to the Royal Society a paper on the manufacture of glass for optical purposes, containing much curious and valuable information upon the subject generally, and which should be consulted by those who are concerned in that difficult branch of the art of glass-making. He successfully availed himself of the use of *borate of lead* as one of its components, when a very dense and highly refractive glass was required, and of this he has lately availed himself in his researches relating to the influence of magnetism upon a polarised ray. (See note, p. 258.) I am indebted to him for the following analyses of different specimens of flint-glass. (*Phil. Trans.*, 1830.)

Silica	51.93	...	48.24	...	44.30
Oxide of lead	33.28	...	40.12	...	43.05
Potassa	13.77	...	10.60	...	11.75
Alumina	0.47	...	0.58	...	0.50
Oxides of iron and manganese	0.27	...	0.08	...	0.12
	<hr/>		<hr/>		<hr/>
	99.72		99.62		99.72

* In the manufacture of all common glass a proportion of broken glass is usually mixed up with the raw materials, and is technically known under the name of *Cullet*.

Kane gives the following tabular view of the composition of several kinds of glass. (*Elem. Chem.*, 720.)

Constituents.	Hard White Glass.		Crown Glass.		Bottle Glass.		Crystal.	Flint Glass.	
	1.	2.	3.	4.	5.	6.	7.	8.	9.
Silica	71·7	69·2	62·8	69·2	60·4	53·5	59·2	51·9	42·5
Potassa	12·7	15·8	22·1	8·0	3·2	5·5	9·0	13·8	11·7
Soda	2·5	3·0	3·0
Lime	10·3	7·6	12·5	13·0	20·7	29·2	0·5
Alumina ...	0·4	1·2	3·6	10·4	6·0	1·8
Magnesia	2·0	} 2·6	0·6	0·6
Oxide of iron	0·3	0·5		1·6	3·8	5·8	0·4
Oxide of manganese	0·2	1·0
Oxide of lead	8·2	33·3	43·5
	98·1	99·3	100·0	99·0	99·1	100·0	97·8	99·0	100·0

No. 1 is the hard difficultly fusible Bohemian glass ; No. 2 is ordinary Bohemian glass, more fusible than No. 1 ; No. 3 is English ; and No. 4 German glass ; Nos. 5 and 6 are French ; Nos. 7 and 8 English glass ; and No. 9 is Guinand’s glass, for optical purposes. Some of the common green bottle-glass is little else than an impure silicate of lime, and is generally easily acted upon by acids. I have seen conical concretions, in a wine bottle used for holding dilute sulphuric acid, composed of layers of silica and sulphate of lime, the glass being very thin, and even in places perforated at the base of each concretion ; and Warrington has since remarked the same thing, as affecting the flavor of wine; he has given the following comparative analyses of common good bottle glass, and of that with excess of lime. (*Mem. Ch. Soc.*, ii. 248.)

	Good.	Bad.
Silica	59·00	49·00
Lime	19·90	24·75
Soda	10·00	7·25
Potash	1·70	2·00
Oxide of iron	7·00	10·10
Alumina	1·20	4·10
Magnesia	0·50	2·00
Oxide of manganese	trace	trace
	99·30	99·20

The art of coloring glass, and of making artificial gems, is of an old date, and effected by metallic oxides. The paste for artificial gems generally contains borax, and should be kept in fusion till perfectly clear. The following proportions are recommended by M. Douault-Wieland. (*Ann. Ch. et Ph.*, xix. 57.)

	Grains.
Powdered rock-crystal	4056
Red lead	6300
Pure potassa	2154
Borax	276
White arsenic	12

M. Lançon gives the following as ingredients for a good paste :

	Grains.
Litharge	100
White sand	75
White tartar or potash	10

The metals employed as coloring materials are: 1. Gold. The purple of Cassius imparts a ruby tint. 2. Silver. Oxide or phosphate of silver gives a yellow color. 3. Iron. The oxides of iron produce blue, green, yellow, and brown, depending upon the state of oxidizement and quantity. 4. Copper. The oxides of copper give a rich green ; they also produce a red when mixed with a small proportion of tartar, which tends partially to reduce the oxide. 5. Antimony imparts a rich yellow. 6. Manganese. The black oxide of this metal, in large quantities, forms a black glass ; in smaller quantities, various shades of purple. 7. Cobalt, in the state of oxide, gives beautiful blues of various shades ; and with the yellow of antimony or lead it produces green. 8. Chrome produces fine greens and reds, depending upon its state of oxidizement.

White Enamel, is merely glass, rendered more or less milky or opaque by the addition of oxide of tin ; it forms the basis of many of the colored enamels, which are tinged with the metallic oxides. Directions for the preparation of several good *enamel-colors* are given by Mr. Wynn, in the *Transactions of the Society of Arts*, 1817, and *Phil. Mag.*, li.

Avanturin Glass, manufactured at Murano near Venice, derives its glittering appearance from minute crystals of metallic copper, which form beautiful microscopic objects. (LIEBIG, *Ann. der Chem. und Pharm.*, 1843.) By heating for twelve hours a mixture of 300 parts of broken glass, 40 of protoxide of copper, and 80 of iron-scales, and allowing it to cool slowly, the resulting vitreous mass contains numerous minute octohedral crystals of metallic copper. (FREMY and CLEMANDOT, *Comptes Rendus*, Feb. 1846.)

The following are the best authorities upon the subject of colored glasses and artificial gems: NERI, *Art de la Verrerie* ; KUNCKEL ; FONTANIEU, *Encyclopédie Méthodique* ; *Ann. Ch. et Ph.*, xiv. 57 ; AIKIN'S *Dictionary*, Art. GLASS ; LARDNER'S *Cyclopædia* ; DUMAS' *Chim. app. aux Arts*.



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